JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC CHEMISTRY.

1898. Vol. LXXIV. Part I.

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1898.

RICHARD CLAY AND SONS, LIMITED,
LONDON AND BUNGAY

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART I.

Organic Chemistry

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

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1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus :— *Annalen*, **221**, 92, instead of ccxxi, 92.

5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

6. As a rule, details of methods of preparation or analysis, or, generally speaking, of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

Nomenclature.

7. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radiclos with the group

OH, *hydroxides* and not hydrates ; for example, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation. Compounds such as CH_3ONa, C_2H_5ONa, $C_7H_{15}ONa$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ.*

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3{\cdot}[CH_2]_5{\cdot}CH_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane ; for example, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ = propylmethane ; $CH_3{\cdot}CH(CH_3)_2$ = isopropylmethane or trimethylmethane ; or, although less frequently, by names such as di-isopropyl.

11. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $C_nH_{2n+1}{\cdot}CH{:}CH{\cdot}C_nH_{2n+1}$ as α-, and those of the form $CH_2{:}C(C_nH_{2n+1})_2$ as β-compounds, thus : $CH_3{\cdot}CH{:}CH{\cdot}CH_3$ = α-dimethylethylene ; $CH_2{:}C(CH_3)_2$ = β-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH{\vdots}C{\cdot}C_nH_{2n+1}$ and $C_nH_{2n+1}{\cdot}C{\vdots}C{\cdot}C_nH_{2n+1}$. Adopt the name *allene* for the hydrocarbon $CH_2{:}C{:}CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol* ; such as quinol, catechol, resorcinol saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by, names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol ; furfuraldehyde instead of furfurol ; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5{\cdot}OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oil*, as anisoil and anethoil.

Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not oxy-derivatives ; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_5O, C_6H_5O, $CH_3{\cdot}COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3:4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2{\cdot}COOH$, and not $C_6H_3(OC_2H_5)_2{\cdot}COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2{\cdot}COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

15. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic* acids, or failing this, *sulpho-compounds*: as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2{\cdot}NH_2$ should be termed sulphonamides.

16. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as, morphine hydrochloride and not morphine hydrochlorate.

Notation.

17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^α for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr_β for $CH(CH_3)_2$, Ph for C_6H_5, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:

$$CCl_3{\cdot}CH(OEt)_2 \text{ instead of } CCl_3{-}CH{<}{\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}}$$

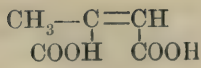
$$[CCl_3{\cdot}CH(OH)]_2S \text{ instead of } {\begin{matrix}CCl_3{-}CHOH\\CCl_3{-}CHOH\end{matrix}}{>}S$$

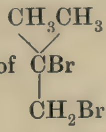
$$CH_2{:}CH_2 \text{ instead of } CH_2{=}CH_2$$

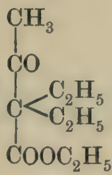
$$CH{\vdots}CH \text{ instead of } CH{\equiv}CH$$

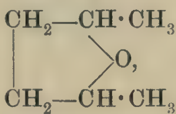
$$CH{\vdots}C{\cdot}CH_2{\cdot}CH_2{\cdot}C{\vdots}CH \text{ instead of } \begin{matrix}CH_2{-}C{\equiv}CH\\ |\\ CH_2{-}C{\equiv}CH\end{matrix}$$

$$CHMe{:}CHPr^\alpha \text{ instead of } CH_3{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3,$$

COOH·CH:CHMe·COOH instead of 

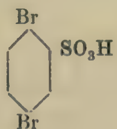
$CH_2Br·CBrMe_2$ instead of 

$CEt_2Ac·COOEt$ instead of 

$\left.\begin{matrix} CH_2·CHMe \\ CH_2·CHMe \end{matrix}\right\rangle O$ instead of 

CHPh(OBz)·CH(OBz)·COOEt instead of
$C_6H_5·CH(O·CO·C_6H_5)·CH(O·CO·C_6H_5)·COOC_2H_5$.

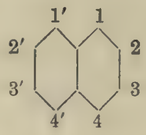
19. In representing the constitution of benzene derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example :—

Paradibromobenzenesulphonic acid, $C_6H_3Br_2·SO_3H$ [Br : SO_3H : Br = 1 : 2 : 4] instead of  the figures always being used in the order 

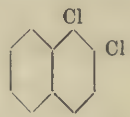
Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them ortho- or meta-dibromobenzene, &c.

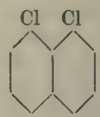
20. Moreover, in representing the constitution of derivatives of other "closed chain" hydrocarbons, do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner :—

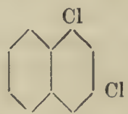
In the case of naphthalene, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1′, 2′, 3′, 4′ in the order shown by the annexed symbol :—

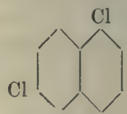


The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene [Cl : Cl = 1 : 2], &c., thus :—

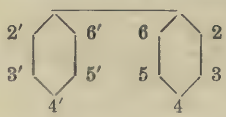
1 : 2 dichloro-naphthalene = 

1 : 1′ dichloro-naphthalene = 

1 : 3 dichloro-naphthalene = 

1 : 3′ dichloro-naphthalene = 

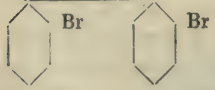
In the case of diphenyl, indicate the position of the radicles relatively to the carbon-atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2′, 3′, 4′, 5′, 6′, as shown by the following symbol :



Thus the mono-derivatives, the bromodiphenyls, for example, are represented as

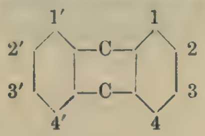
Bromodiphenyl [Br = 2]
,, [Br = 3]
,, [Br = 4]

and the two dibromodiphenyls  and

 are respectively dibromodiphenyl [Br : Br = 2 : 3]

and dibromodiphenyl [Br : Br = 2 : 6.′]

In the case of anthracene, employ the following symbol and indicate the position of the radicles relatively to the central C_2-group :



Examples :

Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 2].
Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 4].
Anthraflavic acid, $C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$ [OH : OH = 2 : 3′].

Purpurin, $C_6H_4 : C_2O_2 : C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

In speaking of compounds such as these, their constitution may be represented by the names

1 : 2 Dihydroxyanthraquinone	=	Alizarin.
1 : 4 ,,	=	Quinizarin.
2 : 3′ ,,	=	Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquione	=	Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

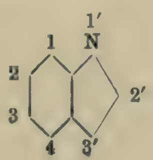
21. *In the case of thiophen,* express the position of the radicles introduced relatively to the sulphur atom by numbers, as shown by the following symbol :

In the cases of pyrroline and pyridine, indicate the position relatively to the nitrogen atoms as shown by the following symbols :

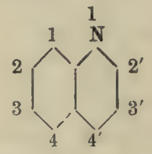
Pyrroline.

Pyridine.

In the case of indole, positions should be numbered as shown in the following symbol :—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1′, 2′, 3′, 4′, in the order shown by the annexed symbol :—



The Editor's decision, in all matters connected with the Abstracts, must be considered final.

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Orders of Isomerism among Homologous Paraffins. By Sima M. Losanitsch (*Ber.*, 1897, **30**, 1917—1926).—The author has elaborated a table which indicates the number of possible isomerides for each member of the methane series from CH_4 to $C_{20}H_{42}$. By a system of analysis which is explained in the paper, the number of isomerides belonging to each order of isomerism has been calculated and recorded in separate columns of the table. M. O. F.

The Formation of Natural Petroleum and the Spontaneous Polymerisation of Hydrocarbons. By Carl Engler (*Ber.*, 1897, **30**, 2358—2365).—The supposition that the natural petroleums have, as a rule, been formed by the distillation under pressure of fats derived from animal organisms, accounts for the fact that these oils contain extremely little nitrogen. It, however, does not appear to account for the high molecular weight, boiling point, and specific gravity of the constituents of the oil, since in all experiments which have been made on the distillation of fats, the product has consisted mainly of low boiling, light hydrocarbons. The author proposes to ascribe this to the gradual polymerisation of the light hydrocarbons which form the first product of the distillation, and has examined a number of distillates derived from various sources for evidence in favour of such a gradual change in density. Samples of Galician petroleum were found to increase in specific gravity by 0·0011—0·0015 in about three weeks, whilst petroleum from Java increased by 0·01 in a few days. Similar results were obtained with distillates from coal tar and brown-coal tar. Finally, the fractions obtained by the distillation of fats under pressure were

proved to behave in a similar manner. The sp. gr. of one set of samples increased by about 0·002 in a month, whilst five other specimens which had been preserved for nine years had increased in sp. gr. during that time by 0·016. It appears probable, therefore, that the comparatively high specific gravity of the constituents of natural petroleum has been acquired in this way during the extended period which has elapsed since the first production of the material. A. H.

Formation of Olefines, Naphthenes, and Benzene Hydrocarbons by the Distillation of Fats under Pressure. By CARL ENGLER and TH. LEHMANN (*Ber.*, 1897, **30**, 2365—2368).—The distillate obtained by heating fish oil under pressure contains about 37 per cent. of olefines, which will combine with bromine or sulphuric acid. These are apparently mixtures of the various members of the series from hexylene up to nonylene. The presence of naphthenes could not be proved with certainty, but the composition of the various fractions after the removal of olefines and benzene derivatives appeared to point to the presence of small amounts of these hydrocarbons along with the paraffins. The benzene derivatives were recognised by conversion into their nitro-compounds, benzene, toluene, metaxylene, mesitylene, and pseudocumene being all detected. A. H.

Purification of Commercial Acetylene. By GEORG LUNGE and EDUARD CEDERCREUTZ (*Zeit. angw. Chem.*, 1897, 651—655).—(See this vol., ii, 54.)

Rutheniocyanides. By JAS. LEWIS HOWE (*J. Amer. Chem. Soc.*, 1896, **18**, 981—987. Compare Abstr., 1894, ii, 386).—A better yield of potassium rutheniocyanide, $K_4RuC_6N_6 + 3H_2O$, is obtained when potassium cyanide is fused with potassium ruthenionitrosochloride than when the ammonium salt is used. A good yield may also be obtained by fusing ruthenium with potassium hydroxide, dissolving the melt in water, and then boiling with potassium cyanide. Other methods were tried, but the amount of rutheniocyanide formed was extremely small. A number of reactions of rutheniocyanides are enumerated. Lead acetate gives a fine, white precipitate, soluble in nitric acid; silver nitrate, a white, curdy precipitate, insoluble in ammonia or nitric acid; ferric chloride, a rich purple precipitate which is soluble in water, but is reprecipitated by salts or alcohol; ferrous sulphate, a pale green precipitate changing to violet, and copper sulphate, a pale green, flocculent precipitate. Bromine changes the solution to a dark red; nitric acid has no action in the cold, but on gently heating reddens the solution.

Two methods of purification applicable to such portions of rutheniocyanides as cannot be separated by crystallisation are given.

A substance crystallising in thick, straw-coloured, hexagonal plates was obtained by boiling potassium ruthenionitrosochloride with a strong solution of potassium cyanide; this compound is still under investigation.

Barium rutheniocyanide, $Ba_2RuC_6N_6 + 6H_2O$, obtained from the potassium salt, crystallises in pale, straw-coloured, diamond-shaped

monoclinic crystals slightly soluble in cold water. It loses $5\frac{1}{2}H_2O$ at 100°, and the remaining $\frac{1}{2}H_2O$ at about 200°. J. J. S.

Does the Volume of a Liquid Change in Consequence of Alcoholic Fermentation? By TÁMAS KOSUTÁNY (*Landw. Versuchs.-Stat.*, 1897, **49**, 173—183).—The results of the author's experiments indicate that the volume of a saccharine liquid is not altered by fermentation, and that the volume of the sugar which is decomposed is the same as that of the alcohol produced. It is probable that the volume of the carbonic anhydride formed, considered as a liquid, is the same as that of the decomposed sugar and the newly formed alcohol; that is to say, 1 vol. sugar = 1 vol. alcohol = 1 vol. liquid carbonic anhydride. N. H. J. M.

Preparation of Ether Free from Alcohol. By P. FRITZSCHE (*Zeit. anal. Chem.*, 1897, **36**, 298—302).—Ethyl hydrogen sulphate, when heated with sulphuric acid at 130—140°, yields only traces of ether, whilst at higher temperatures sulphurous anhydride and ethylene are evolved. (Compare Graham, *Annalen*, 1850, **75**, 108, and Buignet, *J. Pharm.*, 1850, [iii], **18**, 130.) If the mixture is diluted with 10 per cent. of water, small quantities of ether and alcohol are obtained, and if a larger proportion of water is used more ether is obtained, but it is always mixed with large quantities of alcohol. When the amount of water exceeds 50 per cent., ether is no longer formed, and alcohol is the sole product. The author recommends the following method for the preparation of ether free from alcohol. Four flasks, A, B, C and D, are so connected that the gas which is evolved from A passes through a tube leading nearly to the bottom of B, the other flasks are connected in a similar manner, and D in its turn is connected with a good condenser. An equal quantity of ethyl hydrogen sulphate or mixture of alcohol and sulphuric acid is placed in each flask, water is added to A, B and C so that A contains 33 per cent. of water, B 22 and C about 10 per cent. A is strongly heated and B gently, C and D are gently heated as the ether begins to distil over from B. The contents of D should not increase to any appreciable extent, C should show a slight, and B a considerable, increase. When A yields no more vapours, its contents are removed and replaced by those of B. Similarly, those of C are passed into B, and those of D into C, a fresh supply of ethyl hydrogen sulphate being placed in D. In the usual preparation of ether by running alcohol into a heated mixture of alcohol and sulphuric acid, the vapours which pass over can be freed from alcohol by making them pass through a small flask containing ethyl hydrogen sulphate or even sulphuric acid. J. J. S.

Manufacture of Ethyl Hydrogen Sulphate from Gases Containing Ethylene. By P. FRITZSCHE (*Zeit. anal. Chem.*, 1897, **36**, 303—306).—The gas, coal gas or gas from coke ovens, for example, is freed from tar, ammonia, benzene, and carbon bisulphide and then dried. The drying and removal of condensation products is accomplished by treating the gas with dilute (under 80 per cent.) sulphuric acid at 70—80°. By this means, homologues of ethylene are also removed. The gas is then heated to 110—120° and passed

into the absorption apparatus. This consists of scrubbers kept at 110—120°, and filled with acid-proof stones over which sulphuric acid trickles. Four of five of these are connected in series, the fresh acid being always run into the last scrubber where the gas makes its exit: after leaving this last scrubber, the acid is pumped to the top of the next and so on, until it contains 50—60 per cent. of ethyl hydrogen sulphate. It can then be used for the manufacture of alcohol or ether.

J. J. S.

Nitropropylic Alcohol. By LOUIS HENRY (*Rec. Trav. Chim.*, 1897, **16**, 189—192).—Twenty-five grams of nitroethane are added to a mixture of formaldehyde of 35 per cent. (30 grams) with an equal volume of water; several small pieces of potassium hydrogen carbonate are thrown in, and the mixture is vigorously shaken. The action proceeds slowly, the temperature rises some 30°, and the nitroethane gradually disappears. The products of several experiments are united, extracted with ether, and the ether evaporated; if the residue, after drying in a vacuum over sulphuric acid, is placed in a mixture of ice and salt, the greater part of the nitroisobutylic glycol (Abstr., 1896, i, 4) separates in a crystalline form. The residual liquid is subjected to repeated distillation under diminished pressure, when *β-nitropropylic alcohol*, $NO_2\cdot CHMe\cdot CH_2\cdot OH$, is obtained in the form of a colourless oil boiling at 120—122° under 32 mm. pressure; its sp. gr. $= 1\cdot209$ at 6°; it is readily soluble in ether, or in alcohol and ether. Phosphorus pentachloride converts it into *nitropropylic chloride*, $NO_2\cdot CHMe\cdot CH_2Cl$, boiling at 172—173°.

J. J. S.

Nitro-Alcohols. By LOUIS HENRY (*Rec. Trav. Chim.*, 1897, **16**, 193—207. Compare Abstr., 1896, i, and preceding abstract).—

I. Nitro-alcohols containing C_3.

β-Nitropropylic alcohol, $OH\cdot CH_2\cdot CHMe\cdot NO_2$, and β-nitroisopropylic alcohol, $NO_2\cdot CH_2\cdot CHMe\cdot OH$, have already been described. *γ-Nitropropylic alcohol*, $OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot NO_2$, is obtained by the action of silver nitrite on trimethylenic iodohydrin (next abstract). It is a colourless, somewhat viscous liquid, having a feebly pungent odour, and is readily soluble in water, alcohol or ether. Its sp. gr. $= 1\cdot175$ at 13°, and it distils at 138—140° under 32 mm. pressure. It readily condenses with piperidylcarbinol, $C_5H_{10}:N\cdot CH_2\cdot OH$, yielding a compound, $OH\cdot CH_2\cdot CH_2\cdot CH(NO_2)\cdot CH_2\cdot N:C_5H_{10}$, which crystallises in large needles melting at 70—71°. The *acetate*, $NO_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OAc$, is a colourless liquid boiling at 140—142° under 38 mm. pressure. Its sp. gr. $= 1\cdot191$ at 16°.

II. Nitro-alcohols containing C_5.

β-Nitrodiethylcarbinol, $NO_2\cdot CHMe\cdot CH(OH)\cdot CH_2Me$, is formed by the addition of nitroethane to propaldehyde. It is a colourless liquid with a slight aldehydic odour, and is readily soluble in alcohol or ether. Its sp. gr. $= 1\cdot071$ at 14°, and it boils at 118—121° under 43 mm. pressure. *Methyl-α-nitropropylcarbinol*, obtained by the addition of nitropropane, $CH_2Me\cdot CH_2\cdot NO_2$, to acetaldehyde, distils at 112° under 36 mm. pressure. *Nitromethylisopropylcarbinol*, $NO_2\cdot CH_2\cdot CH(OH)\cdot CHMe_2$, is obtained by the combination of nitro-

methane with isobutaldehyde. Its sp. gr. $=1.096$ at 14°, and it distils at 120—123° under 40 mm. pressure. *β-Nitroisoamylic alcohol*, $OH\cdot CH_2\cdot CH(NO_2)\cdot CHMe_2$, boils at 138—139° under 36 mm. pressure, and its sp. gr. $=1.0966$.

III. Nitro-alcohols containing C_6.

Nitromethylisobutylcarbinol, $NO_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CHMe_2$, formed by the union of nitromethane with isovaleraldehyde, distils at 127—130° (38 mm.), and its sp. gr. $=1.025$ at 14°. *Methyl-α-nitroisobutylcarbinol*, $OH\cdot CHMe\cdot CH(NO_2)\cdot CHMe_2$, obtained from nitroisobutane and acetaldehyde, boils at 119—123° (38 mm.), and its sp. gr. $=1.0533$.

IV. Halogen derivatives of nitro-alcohols.

ββ-Chloronitropropylic alcohol, $OH\cdot CH_2\cdot CCl(NO_2)\cdot CH_3$, obtained by the union of formaldehyde with chloronitroethane, is a colourless oil which solidifies on cooling to large, prismatic needles melting at 13·5°. Its sp. gr. $=1.37$ at 14°, and it boils at 115° under 44 mm. pressure. The corresponding *ββ-bromonitropropylic alcohol*, $OH\cdot CH_2\cdot CBr(NO_2)\cdot CH_3$, melts at 42°. It has been found impossible to obtain iodonitroethane in a pure form. J. J. S.

Trimethylene Derivatives. By LOUIS HENRY (*Rec. Trav. Chim.*, 1897, **16**, 213—217. Compare Abstr., 1897, i, 1).—*Trimethylenic iodohydrin*, $OH\cdot CH_2\cdot CH_2\cdot CH_2I$, obtained by the action of sodium iodide on a solution of the chlorhydrin in methylic alcohol, is a colourless, limpid liquid which turns brown on exposure to sunlight. It is only sparingly soluble in water, but dissolves readily in alcohol or ether. Its sp. gr. $=2.349$ at 13°, and it boils at 115° under 38 mm. pressure, and at 225° under 758 mm. pressure without undergoing decomposition.

Trimethylenic iodacetate, $OAc\cdot CH_2\cdot CH_2\cdot CH_2I$, may be obtained in a similar manner from the corresponding chlorine derivative. It is a colourless liquid with an agreeable odour, boiling at 207—210° under 757 mm. pressure, and at 112—115° under 38—40 mm. pressure. Its sp. gr. $=2.112$ at 13°. J. J. S.

Nitro-Alcohols. By LOUIS HENRY (*Ber.*, 1897, **30**, 2206—2207).—Attempts to prepare nitrotrimethyleneglycol,

$$OH\cdot CH_2\cdot CH(NO_2)\cdot CH_2\cdot OH,$$

by the partial condensation of nitromethane with formaldehyde proved unsuccessful, three molecules of the aldehyde taking part in the reaction, with formation of nitroisobutylglycerol (nitrotrihydroxyisobutane), $NO_2\cdot C(CH_2\cdot OH)_3$ (Piloty and Ruff, Abstr., 1897, i, 453). When bromonitromethane is employed, however, *bromonitrotrimethyleneglycol*, $OH\cdot CH_2\cdot CBr(NO_2)\cdot CH_2\cdot OH$, is formed in colourless crystals. The author hopes to convert this substance into glycerol by reduction, followed by substitution of hydroxyl for the amido-group.

A. H.

Glyceryl Monochlorhydrin from Allylic Alcohol. By LOUIS HENRY (*Rec. Trav. Chim.*, 1897, **16**, 208—212).—Hanriot (*Bull. Soc. Chim.*, **29**, 399) has cast some doubt on the constitution of the compound previously obtained by the author by the addition of hypochlorous acid to allylic alcohol. It is now pointed out that analogy and also the properties of the compound point to the constitution

previously given, namely, $OH\cdot CH_2\cdot CHCl\cdot CH_2\cdot OH$. In similar cases of the addition of hypochlorous acid to propylene derivatives containing the grouping $-CH\colon CH_2$, it has been shown that the chlorine atom attaches itself to the CH-group and the hydroxyl radicle to the CH_2-group. Further, when the monochlorhydrin is reduced with sodium amalgam and water, *a*-propylene glycol, $CH_2(CH_2\cdot OH)_2$, is formed. When the chlorhydrin is oxidised with nitric acid, oxalic acid is the chief product. A better yield of the chlorhydrin is obtained if the crude product is extracted with alcohol and potassium carbonate instead of with ether as previously recommended.

J. J. S.

Constitution of Penterythritol. By GABRIEL GUSTAVSON and Miss O. POPPER (*J. pr. Chem.*, 1897, [ii], **56**, 95—96).—When penterythritol tetrabromhydrin is repeatedly heated at 125° with alcoholic potash until all the bromine has been removed, *penterythritol ethylic ether*, $C(CH_2\cdot OEt)_4$, is the sole product, which fact confirms Tollens' and Wigand's view of the constitution of penterythritol. The ether forms a syrup insoluble in water; it boils at 220—225°, and does not solidify at $-18°$; it has sp. gr. $=0\cdot9229$ at 0°/4°, 0·9082 at 16°/4°, and 0·9017 at 21°/4°; its index of refraction $=1\cdot41647$ at 21°; hydriodic acid hydrolyses it to penterythritol and ethylic iodide.

C. F. B.

Isomaltose. By HERMANN OST (*Chem. Zeit.*, 1896, **20**, 701—702).—In a former paper (*ibid.*, 1895, **19**, 1501), the author brought forward experimental evidence showing that the so-called isomaltose of Lintner is merely impure maltose, and that the osazone obtained from it is identical with maltosazone (compare also Trans., 1895, 702, 709, 739; 1897, 508). He, moreover, expressed his conviction that the synthetic hexabiose (glucobiose), obtained and named isomaltose by E. Fischer (Abstr., 1891, 412), yielded an osazone consisting essentially of maltosazone; it therefore appeared that the synthesis of maltose had been effected. Fischer has, however, since refuted this view (Abstr., 1896, i, 119).

The present paper recounts the author's more recent experiments. Dealing with Lintner's isomaltose, he states that when that portion of the products of starch hydrolysis which is soluble in 95 per cent. alcohol, consisting principally of maltose, is fermented with yeast, the residue does not give the osazone reaction (compare Brown and Morris, Trans., 1895, 729; Ling and Baker, *ibid.*, 1897, 520).

The synthetic isomaltose is best prepared by the action of 33 per cent. sulphuric acid on glucose (and also on maltose) at the ordinary temperature for $4\frac{1}{2}$ months. After neutralisation, the filtered solution is brought to a concentration of 10—12 per cent. and sown with washed and pressed brewery yeast, amounting to half the weight of the glucose used, fermentation being allowed to proceed at 20—25°. On the following day, a fresh quantity of yeast equal in amount to the first is added. No further evolution of carbonic anhydride is observed at the end of 2 days, but the liquid is placed in an incubator at 30° for 3 days. The unfermented residue represents 27 per cent. of the glucose employed, and consists essentially of isomaltose. This iso-

maltose has up to the present only been obtained as a syrup; its specific rotatory power may probably be placed at about $[\alpha]_D = +70°$ and its cupric reducing power (by Sachsse's method) at 58—65 per cent. that of maltose. The osazone was found to have the composition of a hexabiosazone, and after being dried at 100°, it melted at 130—145°; its optical rotatory power in alcoholic solution examined with Auer light was "$[\alpha]_{Auer}$" $= -15°$ to $-20°$. A. R. L.

Analytical Investigation of the Hydrolysis of Starch by Acids. By George W. Rolfe and George Defren (*J. Amer. Chem. Soc.*, 1896, **18**, 869—900; 1897, **19**, 261—263).—The authors' experiments were carried out in a modified autoclave from which quantities of the solution undergoing hydrolysis could be removed at any desired moment. As a rule, about 100 grams of starch were mixed with a litre of water, containing hydrochloric acid, the maximum concentration of the latter being a N/10 solution and the minimum a N/1000 solution. Sulphuric acid and oxalic acid were also used. Samples of 50—75 c.c. of the solution were removed at different stages of the hydrolysis, shaken with an excess of marble dust, and two drops of N/10 sodium hydroxide added. The specific gravity, total solids (by 3·86 divisor), specific rotatory power, and cupric reducing power were then determined in the clear filtrate.

The authors have incidentally determined the relation between angular degrees for sodium light, as furnished by polarimeters of the Laurent type, and divisions of the Ventzke scale, furnished by instruments employing ordinary light and quartz compensation, and find, with standard quartz plates, the usual factor, namely, 0·346, whilst with solutions of glucose they obtained the factor 0·344, which is in agreement with Rimbach's results (Abstr., 1894, ii, 486. Compare Brown, Morris, and Millar, Trans., 1897, 93).

The results point to the fact that the cupric-reducing power of the total product bears a constant relation to the specific rotatory power, even when starch is hydrolysed under widely varying conditions. Hence, given the one, the value of the other can be calculated. To a rotation of about 90°, the plotted results coincide extremely closely with the arc of a circle, the equation of which is $x^2 + y^2 - 758x + 772·4y = 0$, which exactly intercepts the "zero" and "hundred" points at $[\alpha]_D = 195°$ and 53·5° respectively. The curves obtained by plotting the percentages of maltose, dextrin, and glucose as ordinates, and the specific rotatory powers as abscissæ in the same ordinate system are quite as noteworthy.

The dextrin curve gradually falls from 100 per cent. to zero near the rotation corresponding with that of glucose, namely, $[\alpha]_D = 53·5°$, whilst the maltose curve reaches a maximum percentage of 44·1 at about $[\alpha]_D = 129°$, corresponding with the usual state of conversion of commercial glucose and then falls, disappearing at $[\alpha]_D = 53·5°$. The glucose curve steadily mounts to 100 per cent. At the point where the maximum percentage of maltose is present, the glucose and dextrin are present in equal quantity, as shown by the intersection of the curves. The authors have calculated a table from the curves, which gives the values of maltose, glucose, and dextrin within one-

tenth per cent. for successive stages of acid hydrolysis represented by each degree of rotation between $[\alpha]_D = 195°$ and 53·5°.

With the data at hand, the authors sought to determine whether a sample of commercial glucose is a product of one hydrolysis or a mixture of two separate ones. Since in a factory the time occupied in filling a converter is about one-third of the total time required for the hydrolysis, there must be a great difference in the time of hydrolysis of different portions of the starch. Despite this, however, the authors find that samples made in one operation conform to their table, and there appears to be strong evidence that those which depart from it are mechanical mixtures. The authors draw the following conclusions from their results. That in any homogeneous acid-converted starch-product the specific rotatory power corresponds with a definite chemical composition. That but three simple carbohydrates (leaving reversion products out of consideration), possibly in molecular aggregates, exist in a solution of a starch product hydrolysed by acids.

The usual practice in glucose factories of determining the degree of conversion of the starch is by means of the iodine reaction; the tint at which the conversion is considered complete coincides with a solution of the conversion products having a specific rotatory power between the limits of the rotations $[\alpha]_D = 128°$ and 135°. A. R. L.

Soluble Starch. By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1897, **30**, 2108—2110).—It is shown that "soluble starch" is quite different from "amylodextrin," since the former gives a pure blue coloration with iodine, and does not reduce Fehling's solution, whilst the latter gives a reddish-brown coloration with iodine and slowly reduces Fehling's solution. Soluble starch is best prepared by treating rice starch with a small quantity of a 1 per cent. solution of potassium hydroxide, leaving it for some time, then adding excess of the alkali, and heating on the water bath with repeated shaking for from 20—30 minutes; the product is then filtered, rendered slightly acid with acetic acid, and precipitated by the addition of alcohol. It can be purified by repeated dissolution in water and precipitation with alcohol; the snow-white product prepared in this way contains very little ash, and is soluble in water to the extent of about 4 per cent.

J. F. T.

Oxycellulose. By LÉO VIGNON (*Compt. rend.*, 1897, **125**, 448—450). —Oxycellulose is best prepared by the action of potassium chlorate and hydrochloric acid on carefully purified cotton wool. 150 grams of the chlorate is dissolved in 3 litres of water, 30 grams of purified cotton is added, and 125 c.c. of hydrochloric acid of 22° gradually stirred in. The liquid is heated nearly to boiling for about an hour, and the product is washed with water, and finally with alcohol; 87·58 per cent. of the oxycellulose thus prepared dissolves in fused potash at 180°, whereas only 12·0 per cent. of cellulose dissolves. It would follow that the product is a mixture of 75 per cent. of oxycellulose with 25 per cent. of cellulose. On this basis, the composition of the oxycellulose is C, 43·15; H, 5·97, O, 50·65; the formula

$$C_{24}H_{38}O_{21} = (4C_6H_{10}O_5—H_2 + O)$$

requires C, 43·5; H, 5·7; O, 50·7.

The heats of combustion are, cellulose 4190 to 4224, oxycellulose 4124 to 4133; the heat developed by immersion in normal potassium hydroxide solution is, cellulose 0·74, oxycellulose 1·30 Cal. per 100 grams, and hence the energy of the acidic function has increased. The power of absorbing colouring matters such as safranin or methylene blue has also greatly increased.

Oxycellulose dissolves in aqueous potash, yielding a golden-yellow solution, which reduces Fehling's solution; it gives a white precipitate when acidified with hydrochloric acid. The oxycellulose itself energetically reduces Fehling's solution, but the residue left after extracting with hot potassium hydroxide solution has lost this reducing power. With Schiff's reagent, oxycellulose gives an intense violet coloration, and therefore has an aldehydic function. C. H. B.

Aliphatic Nitramines. By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1897, **16**, 226—228. Compare Bamberger, Abstr., 1897, i, 468).—A mixture of methylnitramine with potassium nitrite in molecular proportion reacts in aqueous solution, yielding nitrogen, potassium nitrate, methylic alcohol, and the two isomeric dimethylnitramines. Small quantities of carbonic anhydride and of an extremely volatile oil with an isonitrilic odour are obtained as byeproducts. The author considers that this decomposition is best represented by supposing an additive compound, $NO_2 \cdot NMe \cdot N(OH)_2$, to be first formed by the union of the nitrous acid with methylnitramine. It follows that methylnitramine is capable of oxidising nitrous to nitric acid.

The author also finds that colours similar to that mentioned by Bamberger as being produced by the action of zinc dust and acetic acid on a solution of benzenediazoic acid and α-naphthylamine are also produced by aliphatic nitramines when their acetic acid solutions are mixed with zinc and α-naphthylamine, aniline, dimethylaniline, or phenylenediamine. J. J. S.

Cystin. By CAMILLE CHABRIÉ (*Compt. rend. Soc. Biol.*, 1896, [x], **3**, 72—73).—Külz showed that cystin may originate during the pancreatic digestion of proteids, and this suggested that it may be formed by the action of hydrogen sulphide on amido-acids. In carrying out the investigation, the gas was passed through a mixture of aldehydeammonia with ether, and a crystalline substance, soluble in ether and melting at 60—63°, was obtained of the constitution

$$SH \cdot CHMe \cdot NH \cdot CHMe \cdot OH.$$

The appearance of this new substance is held to be confirmatory of the hypothesis stated above concerning the origin of cystin.

W. D. H.

Volatilisation of Lactic Acid and its Anhydrides at the Ordinary Temperature; Volatilisation of Lactic Acid with Water Vapour. By JOSEPH A. MULLER (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1206—1210).—When solutions of lactic acid are evaporated to dryness in a vacuum over sulphuric acid, and then kept in a vacuum over solid potash, part of the acid is converted into anhydride, and part volatilises, the loss in four days amounting to 0·0112 gram, and in 11 days to 0·0217 on an original quantity of 0·1280 gram. Similar results were obtained with ethereal solutions of the acid. The rate

of evaporation is lower the higher the proportion of lactic anhydride present; the anhydride itself is practically non-volatile in a vacuum at the ordinary temperature. Lactide, on the other hand, is distinctly volatile; 0·1406 gram lost 0·0046 gram in 13 days, and 0·0246 gram in 49 days.

Boiling solutions of lactic acid lose only a small quantity of the acid, and the loss is directly proportional to the quantity of acid in the solution. The loss of lactic acid when more or less concentrated solutions are exposed to dry air or in a dry vacuum is not due to mechanical removal with the water vapour, but must be attributed to the volatility of the acid itself. This volatility introduces noteworthy errors into the estimation of lactic acid in wines when the latter are evaporated to dryness. (Compare this vol., ii, 57.)

C. H. B.

Formation of Chains. XIV. Aniline and Ethylic Salts of Fatty Brominated Acids. By CARL A. BISCHOFF (*Ber.*, 1897, **30**, 2303—2310).—This investigation was carried out with the object of determining whether the conditions which regulate the formation of carbon chains were applicable to the formation of carbon-nitrogen chains, and it was found, as far as the investigation was carried, that double alkyl groups, such as isopropyl, isoamyl, &c., have precisely the same effect in the latter case as in the former. During the course of the investigation, *ethylic a-anilidobutyrate*, which had previously only been obtained as an oil, was isolated as a colourless, crystalline substance melting at 29°.

J. F. T.

Formation of Chains. By CARL A. BISCHOFF (*Ber.*, 1897, **30**, 2310—2315). **XV. Aniline and Fatty Brominated Acid Amides.**—Bromacetamide reacts more readily with aniline than the chlorinated derivative, the reaction taking place at a much lower temperature, and if this be not allowed to exceed 130°, *phenylimidodiacetamide*, $NPh(CH_2{\cdot}CO{\cdot}NH_2)_2$, is obtained in nodular masses melting at 225°; if, however, the reaction be carried out at 170°, *phenylimidodiacetimide* melting at 159° is formed. *a-Bromopropionamide*, $CHBrMe{\cdot}CO{\cdot}NH_2$, prepared in an analogous manner to bromacetamide, crystallises from benzene in slender leaflets melting at 123°, and on condensation with aniline at 98° yields α-anilidopropionamide and at 180° α-anilidopropionanilide. *a-Bromobutyramide*, $CHBrEt{\cdot}CO{\cdot}NH_2$ crystallises from acetone in needles melting at 112°, and yields α-anilidobutyramide on condensation with aniline, the corresponding anilide being formed in small quantity only. *a-Bromisobutyramide*, $CBr{\cdot}Me_2CO{\cdot}NH_2$, melting at 148°, condenses with aniline with the formation of an anilidoisobutyramide melting at 136°; this, however, is the β-derivative, and identical with the compound obtained by Tiemann from anilidoisobutyronitrile.

J. F. T.

Formation of Chains. XVI. Formation of Acid Anilides. By CARL A. BISCHOFF (*Ber.*, 1897, **30**, 2315—2322).—After it had been shown (compare preceding abstracts) that the formation of anilides from anilido-fatty acids according to the equation

$$2NH_2Ph + CBr(a)(b){\cdot}CO{\cdot}NH_2 = NHPh{\cdot}C(a)(b){\cdot}O{\cdot}NHPh + NH_4Br,$$

only occurred when $a = CH_3$ and $b = H$, and not when $a = C_2H_5$, or a and $b = CH_3$, similar experiments were tried with the α-bromo-fatty

amides and aniline, and it was found that the general result was the same. J. F. T.

Preparation of Diethylic Malonate. By WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1896, **18**, 1105—1106).—The preparation of diethylic malonate is very much shortened if sulphuric acid is used instead of hydrochloric, and sodium hydrogen carbonate instead of potassium carbonate. Sodium hydrogen carbonate (90 grams) is added to a warm solution of chloracetic acid (100 grams) in water (200 c.c.), and the heating continued until the temperature is 55—60° and effervescence has nearly ceased; coarsely powdered potassium cyanide (80 grams) is then added, the whole kept well stirred, and the solution quickly evaporated until the temperature reaches 130—135°. When cold, the mass is broken up and transferred to a litre flask containing 40 c.c. of alcohol and connected with a reflux condenser. A well cooled mixture of 160 c.c. of alcohol and 160 c.c. of concentrated sulphuric acid is slowly added, the operation taking 5—10 minutes instead of 1—1½ days as in the old method, and the action is completed on the water bath. The mixture is cooled, well shaken, and water (200 c.c.) added; the undissolved crystals are collected and well washed with ether, the ethereal washings being used for extracting the filtrate. The ethereal solution after being washed with excess of sodium carbonate solution is distilled, when it yields nearly pure ethylic malonate. J. J. S.

Action of Acid Anhydrides on Acids and their Salts. Formation of Ketodilactones, Ketonic Acids and Ketones. By RUDOLPH FITTIG (*Ber.*, 1897, **30**, 2145—2150).—When tricarballylic acid is heated with acetic anhydride, a compound of the formula $C_7H_8O_4$ is obtained, which is readily soluble in chloroform, melts at 98° and is neutral, but when boiled with bases yields salts of the dibasic acid, $C_7H_{10}O_5$. This neutral substance appears to be identical with the ketodilactone, $CO{<}\begin{matrix}O\text{—}CMe\cdot O\\ CH_2\cdot \overset{|}{C}H\cdot CH_2\end{matrix}{>}CO$, described by Emery (Abstr., 1897, i, 325). It seems to be formed by the direct displacement of the hydrogen atom of the CH group in tricarballylic acid by the acid radicle, carbonic anhydride and water being subsequently eliminated. Thus, butyric anhydride produces an analogous *compound*, $C_9H_{12}O_4$, which melts at 55°; benzoic anhydride reacts in a similar manner, and the *compound* formed melts at 137°. The production of this substance shows that the reaction proceeds in the manner indicated above, and not by the formation of a mixed anhydride of tricarballylic acid, from which the ketodilactone might result by loss of water and carbonic anhydride. When tricarballylic acid, in the form of the sodium salt, is heated with acetic anhydride and benzaldehyde, the *benzylidene* derivative of the ketodilactone, $C_7H_6O_4{:}CHPh$, is formed, which crystallises in lustrous plates melting at 160°. In the presence of valeraldehyde or heptaldehyde, on the other hand, the compound $C_7H_8O_4$ is formed.

This direct substitution of an acid radicle for hydrogen is not limited to tricarballylic acid, for acetic anhydride and other anhydrides act in a similar manner with various other acids. Thus, acetic

anhydride reacts very violently with sodium succinate at 130°, the whole mass becoming carbonised, whilst both in this case and when the free acid is employed, a small amount of levulinic acid is produced. A similar violent action occurs between acetic anhydride and sodium itaconate.

It seems probable that the production of hydrochelidonic acid, from succinic anhydride, and the formation of ketones by the action of phosphoric anhydride on the fatty acids, and by the action of acetic anhydride on the fatty acids and their salts, may be brought about in a similar manner. Further investigations are being made into the course of the reaction. A. H.

Rupture of the Carbon Chain in Ethylic Dicarboxyglutaconate (Ethylic $\omega_2\omega_2'$-Propenetetracarboxylate). By MAX GUTHZEIT and HERBERT W. BOLAM (*J. pr. Chem.*, 1896, [ii], **54**, 359—376).—Alkaline hydrolysing agents act on ethylic dicarboxyglutaconate quite differently from acids; on hydrolysis with alkaline hydroxides, this ethylic salt is partially split up into malonic and formic acids, whereas no rupture of the chain takes place when it is treated with acids.

With barium hydroxide, using a 10 per cent. solution, 25 per cent. of the salt is decomposed, and with a 20 per cent. solution 50 per cent. With potassium hydroxide, when 3 mols. of the hydroxide are used, and the hydrolysis conducted at the boiling point of the solution, 30 per cent. of the ethylic salt is decomposed, although a 20 per cent. solution of the hydroxide allowed to remain in contact with the ethylic salt at the ordinary temperature for some weeks does not cause any rupture of the chain.

Barium hydroxide (25 per cent. solution) hydrolyses ethylic benzyldicarboxyglutaconate even at 100°, almost quantitatively to benzylglutaconic acid, only a small quantity of malonic acid being formed.

When treated with acids, ethylic dicarboxyglutaconate is hydrolysed without any decomposition of the acid taking place. Hydrochloric acid gives the best result, 50—60 per cent. of the theoretical yield of dicarboxyglutaric acid being obtained by this means. J. F. T.

Thioureas. By ERNST A. SCHMIDT (*Arch. Pharm.*, 1897, **235**, 435—441).—Bromo- and iodo-thiosinamine have been shown to be derivatives of ψ-propylenethiourea which has been obtained by Gabriel from thiosinamine by intramolecular change. The physiological action of these three compounds is very similar, and hence confirms this relationship of chemical constitution. The halogen derivatives are, in spite of their much higher molecular weight, a little more active than ψ-propylenethiourea itself.

The three isomeric substances thiosinamine, ψ-propylenethiourea, and trimethylenethiourea differ distinctly in their physiological effects.
E. W. W.

Ethylenethiourea and Trimethylenethiourea. By WALTER SCHACHT (*Arch. Pharm.*, 1897, **235**, 441—468).—Ethylenethiourea prepared by Hofmann's method (this Journal, 1872, 501), melts at 194° according to the author. By mixing aqueous solutions of this sub-

stance and of mercuric chloride, a double compound, $2C_3H_6N_2S, 3HgCl_2$, is formed. Compounds of the following composition were also prepared in a similar way: $(C_3H_6N_2S)_3,AgCl$, $(C_3H_6N_2S)_2,PtCl_4$, $(C_3H_6N_2S)_2,Cu_2Cl_2$, $(C_3H_6N_2S)_2,Hg(CN)_2$. Ethylenethiourea also unites with silver nitrate and with gold chloride to form compounds $C_3H_6N_2S,AgNO_3$ and $(C_3H_6N_2S)_2,AuCl$; both these, when treated with picric acid, yield compounds having the formula $C_3H_5N_2SAg,C_6H_2(NO_2)_3OH$ and $(C_3H_6N_2S)_2,AuOC_6H_2(NO_2)_3$ respectively. By triturating ethylenethiourea with mercury, or with finely divided silver or copper, in the presence of alcohol, the alcoholic extract, after separation of the unchanged ethylenethiourea, does not crystallise but contains the metal, and yields a flocculent precipitate with picric acid. The compound with methylic iodide, $C_3H_6N_2S,MeI$, crystallises in transparent, hexagonal prisms, easily soluble in water and chloroform, and melting at 145°; the corresponding *methochloride* obtained by treating the iodide with silver chloride, forms rhombic crystals and melts at 92°. Its *platinochloride*, $(C_3H_5N_2SMeCl)_2,PtCl_4$, crystallises in small, red crystals and melts at 178°; the *aurochloride* in yellow needles melting at 194°, and the picrate in yellow needles melting at 180°. The *ethiodide* is less stable and more hygroscopic, melts at about 157°, the corresponding *platinochloride* at 174°, and the aurochloride at 142°.

From the methochloride, the free base was obtained as a viscid alkaline liquid by the action of sodium hydroxide; the aurochloride prepared from this melted at 194°, and was identical with the aurochloride obtained from the product of the action of methylic iodide on ethylenethiourea silver nitrate by means of silver chloride. In the metallic salts and the halogen compounds, therefore, the metal and the alkyl group are assumed to be directly united to sulphur by displacement of the hydrogen of the SH group. In ethylenethiourea this acid group is supposed to counterbalance the basic character of the nitrogen groups, whereas when the hydrogen of this group has undergone substitution, the basic character is developed, and salts with picric acid may be prepared.

The ethylenic bromide compound, $(C_3H_6N_2S)_2,C_2H_4Br_2$, which crystallises in brown, transparent needles, decomposes without melting, and yields an aurochloride, a platinochloride and a picrate which are not crystalline. The corresponding chlorine compound was prepared from the bromide, and its platinochloride and aurochloride obtained as amorphous precipitates. By the action of concentrated fuming hydrochloric acid or concentrated sulphuric acid at 150°, ethylenethiourea is decomposed with liberation of hydrogen sulphide and sulphur and formation of ethylenediamine hydrochloride. Trimethylenethiourea forms double compounds which are very similar to those of ethylenethiourea, and with mercury, silver, and copper it undergoes a similar reaction. Fuming hydrochloric acid and sulphuric acid effect decomposition with greater difficulty than in the case of ethylenethiourea. E. W. W.

Ketopentamethylene from Vinyltrimethylene Bromide. By Gabriel Gustavson and Miss H. Bulatoff (*J. pr. Chem.*, 1897, [ii],

56, 93—95).—The ketone which is formed, together with an aldehyde, when vinyltrimethylenic bromide (Abstr., 1896, i, 669) is heated with lead oxide and 10—15 parts of water for 6 hours at 135—140°, has been identified as ketopentamethylene, C_5H_8O. No doubt the aldehyde is first formed, and then undergoes a transformation into the ketone; this transformation of a trimethylene into a pentamethylene derivative is noteworthy. The formation and reactions of "vinyltrimethylene" can be equally well, perhaps better, explained by regarding it as methylenetetramethylene, $CH_2{<}{}^{CH_2}_{CH_2}{>}C{:}CH_2$. C. F. B.

Electrolytic Reduction of Nitrobenzene. By WALTHER LÖB (*Zeit. Elektrochem.*, 1897, 3, 471—474).—The experiments were undertaken in the hope of obtaining amidobenzoic acids in analogy with Gattermann's preparation of amidophenols by electrolytic reduction of nitro-compounds in sulphuric acid solution, or with the author's synthesis of chlorinated or brominated anilines by reduction of the nitrobenzenes in solutions containing hydrochloric or hydrobromic acids (Abstr., 1896, i, 605). A solution of nitrobenzene in 4 parts of formic acid to which a few cubic centimetres of strong sulphuric acid are added, in order to increase the conductivity, surrounds the lead or platinum cathode; the carbon or platinum anode is immersed in dilute sulphuric acid, and the two liquids are separated by a porous partition, the apparatus used being that previously described (Abstr., 1897, i, 331). The reduction is at an end when hydrogen begins to escape. The principal product of the reaction was benzidine formate, 70 per cent. of the theoretical yield being obtained; azobenzene, aniline, and a violet-blue base were also isolated in small quantities. The results were not influenced by the temperature, current density or concentration within the fairly wide limits employed. In acetic acid solution, benzidine is again the principal product, azobenzene and traces of paramidophenol being also formed; the addition of oxalic acid to the acetic acid solution makes practically no difference. In ammoniacal solution containing 10 grams of nitrobenzene, 70 c.c of alcohol, 30 c.c. of strong aqueous ammonia, and 5 grams of ammonium chloride, the products of the electrolytic action were different, 2 grams of hydrazobenzene and 5·5 grams of azobenzene being obtained. T. E.

Phosphates from the Phenols. By WILHELM AUTENRIETH (*Ber.*, 1897, 30, 2369—2381).—Phosphorus oxychloride readily reacts with phenols in presence of aqueous soda to form two series of compounds, the normal phosphates, $PO(OR)_3$, and the diphosphates $PO(OR)_2{\cdot}OH$. The latter are also produced by the hydrolysis of the normal phosphates, and may be converted into chlorides and amides. They are very stable towards acids and alkalis, and many of them are precipitated from aqueous solution by dilute hydrochloric acid. When phenol is treated with phosphorus oxychloride in this manner, triphenylic phosphate and diphenylphosphoric acid [diphenylic hydrogen phosphate] are produced. The latter, when pure, crystallises well, is moderately soluble in water, and melts at 61—62° (compare Rapp, Abstr., 1884, 1337). *Triparatolylic phosphate*, $PO(O{\cdot}C_6H_4Me)_3$, crystallises in white needles

melting at 77—78°. *Diparatolylic phosphate*, $PO(O{\cdot}C_6H_4Me)_2{\cdot}OH$, yields an *amide* which crystallises in nacreous plates melting at 146°, and is almost insoluble in water. *Triparachlorophenylic phosphate* crystallises in lustrous, slender needles melting at 99—100°. *Diparachlorophenylic phosphate* forms lustrous, colourless plates and needles melting at 126—127°; the *sodium* salt crystallises in nacreous plates; whilst the *chloride* forms slender needles, and the *amide* lustrous plates melting at 152°. Tri-β-naphthylic phosphate, has been previously described by Heim (Abstr., 1883, 1108). *Di-β-naphthylic phosphate*, $PO(O{\cdot}C_{10}H_7)_2{\cdot}OH$, crystallises in prisms melting at 147—148°; the *sodium* salt forms lustrous plates. The acid is only sparingly soluble in water and is precipitated from aqueous solution by dilute hydrochloric acid; the *amide* crystallises in lustrous plates, melting at 215°. *Tri-1-chloro-2-naphthylic phosphate* crystallises in slender, white needles, melting at 152°. *Di-1-chloro-2-naphthylic phosphate*, $PO(O{\cdot}C_{10}H_6Cl)_2{\cdot}OH$, forms slender needles and melts at 251°. *Tri-α-naphthylic phosphate* crystallises in lustrous needles melting at 145°.

A comparison of the melting points of the various substances described shows that the normal ethers melt at a lower temperature than the diphosphates and these again at a lower temperature than their amides. A. H.

Nitrosoderivatives of Phloroglucinol Diethyl Ether. By Hugo Weidel and J. Pollak (*Monatsh.*, 1897, 18, 347—378. Compare Abstr., 1897, i, 42).—By the action of potassium nitrite and acetic acid on the diethyl ether of phloroglucinol, Moldauer obtained two isomeric mononitroso-derivatives, which he called α- and β-diethoxyquinoneoximes. He was, however, unable to determine either the position of the nitroso-group or whether the derivatives were true nitroso- or isonitroso-compounds.

The authors find that the two diethoxyquinoneoximes give different products on reduction, and these reduction products give different acetyl derivatives, thus proving Moldauer's statement that the two diethoxyquinoneoximes cannot be stereoisomerides.

With regard to the position of the amido-group in the products of reduction, either it must lie between an ethoxy- and a hydroxyl group or between two ethoxy-groups, thus, $OH{\cdot}C{<}\begin{matrix}C(NH_2){\cdot}C(OEt)\\CH{=\!=}C(OEt)\end{matrix}{>}CH$ or $OH{\cdot}C{<}\begin{matrix}CH{\cdot}C(OEt)\\CH{:}C(OEt)\end{matrix}{>}C{\cdot}NH_2$. This point could not be settled by the action of acetic anhydride, which gave only triacetyl derivatives, but by the action of carbamide on the hydrochlorides of the two reduction products, 3:5-diethoxycarbonyl-2-amidophenol, $CO{<}\begin{array}{l}NH{\cdot}\,C{\cdot}C(OEt){:}CH\\ \qquad\; \| \qquad\qquad\quad\; | \\ O{-\!-}C{-\!-}{-\!-}CH{:}C{\cdot}OEt\end{array}$ was produced in the one case, and a substituted carbamide,

$$OH{\cdot}C{<}\begin{matrix}CH{\cdot}C(OEt)\\CH{:}C(OEt)\end{matrix}{>}C{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

in the other, thus definitely proving the position of the amido-group in the products of reduction, and consequently the position of the nitroso-groups in the phloroglucinol derivatives.

Moldauer showed that both nitroso-derivatives can be further

ethylated, α-diethoxyquinoneoxime with production of ethyl pyriphlorone diethyl ether and a red triethyl ether, whereas β-diethoxyquinoneoxime yields only a triethyl ether. By reduction of these triethoxy-compounds, the authors show that both contain, combined directly to nitrogen, an ethoxy-group which can be eliminated as alcohol; they must therefore be regarded as oxime ethers, and the original substances as isonitroso-derivatives: and Moldauer's α- and β-diethoxyquinoneoximes are respectively 3 : 5-diethoxyorthoquinone-2-monoxime and 3 : 5-diethoxy-paraquinone-4-monoxime.

When ethyl pyriphlorone diethyl ether is treated with reducing agents, the elements of water attach themselves, and the product, the monacetyl derivative of 3 : 5-diethoxy-2-amidophenol, when heated with sulphuric acid, loses acetic acid, and with acetic anhydride, gives a substance identical with the triacetyl derivative of 3 : 5-di-ethoxyorthoamidophenol. Further, on reducing pyriphlorone with tin and hydrochloric acid, the hydrochloride of 3 : 5-diethoxy-2-amido-phenol is obtained. These experiments, together with the fact that the monacetyl derivative of 3 : 5-diethoxy-2-amidophenol, on distillation, loses water with formation of pyriphlorone, shows the latter to be 3 : 5-diethoxyethenyl-2-amidophenol.

The unusual formation of an ethenyl derivative from an oxime by the action of alcoholic potash and ethylic iodide, may be explained by supposing that reduction takes place, a part of the alcohol being oxidised to acetic acid, which unites with the intermediate product of reduction, forming 3 : 5-diethoxyethenyl-2-amidophenol; or 3 : 5-diethoxy-orthoquinoneoxime acts partially as a true nitroso-compound, giving a triethyl ether in which the third ethoxy-group is connected to carbon. Such an ether could be converted into an ethenyl derivative according to the following equation,

$$C_6H_2(OEt)_2{<}{}^{OCH_2Me}_{NO} = C_6H_2(OEt)_2{<}{}^{O}_{N}{>}CMe + H_2O.$$

Certain modifications for the preparation of phloroglucinol diethyl ether are given, by which means almost a quantitative yield of the ether can be obtained and also the bye-products, namely diresorcinol, and the monethyl ether of phloroglucinol, can be isolated.

Phloroglucinol monethyl ether crystallises from benzene in large, colourless, needle-shaped crystals melting at 72—73° (uncorr.). When crystallised from water, it contains $2H_2O$.

2-*Amido*-3 : 5-*diethoxyphenol hydrochloride*, obtained by reducing 3 : 5-diethoxyorthoquinone-2-monoxime, crystallises from dilute hydrochloric acid in glistening needles, which become rose-red and then brown on exposure to the air. When heated to 130°, it decomposes without melting. The free amidophenol could not be obtained on account of the ease with which it decomposes in air. When the hydrochloride is treated with acetic anhydride, a *triacetyl* derivative is obtained, crystallising from light petroleum in needles and melting at 110°—112°. The *monacetyl* derivative crystallises in silken needles melting at 122·5—123·5° (uncorr.).

4-*Amido*-3 : 5-*diethoxyphenol hydrochloride*, obtained by reducing the corresponding paraquinoneoxime, crystallises in long, colourless, glistening monoclinic needles, which decompose at about 140° without melting.

The crystals, using water as a solvent, contain $1 H_2O$. The *triacetyl* derivative separates from light petroleum in colourless, glistening needles melting at 81°—83° (uncorr.).

3 : 5-*Diethoxycarbonyl-2-amidophenol*, prepared by heating carbamide with 2-amido-3 : 5-diethoxyphenol, crystallises from light petroleum in glistening needles which are almost insoluble in water, but readily soluble in boiling alcohol, benzene and ethylic acetate. It melts at 192—195° and can be heated to 250° without undergoing decomposition.

2 : 6-*Diethoxy-4-hydroxyphenylcarbamide*, obtained by the action of carbamide on 4-amido-3 : 5-diethoxyphenol, separates from water acidified with acetic acid in small, glistening, prismatic needles, becoming yellow on drying and melting at 199·5—201° (uncorr.). A. W. C.

Metol [Paramethylamidophenol Sulphate]. By Ludwig Paul (*Zeit. angw. Chem.*, 1897, 171—174).—The photographic developer known as "metol" is shown by the author to be *paramethylamidophenol sulphate*, $[(OH)\cdot C_6H_4\cdot NHMe]_2,H_2SO_4$. The *base*, which crystallises from benzene in needles melting at 85°, when treated with nitrous acid, yields a *nitroso*-derivative crystallising in thick prisms, and when oxidised with lead peroxide yields quinone. The author has not been able to obtain the base by the direct methylation of paramidophenol, but has obtained it by heating parahydroxyglycocine at about 220°.
J. J. S.

2 : 5-Diamidoquinone. By Friedrich Kehrmann and G. Betsch (*Ber.*, 1897, 30, 2096—2103).—The preparation of 1 : 4-diamidoquinone was carried out in the following way: 2-amido-5-nitrophenol, prepared from paranitrodiazobenzeneimide, was reduced by means of tin and hydrochloric acid to hydroxyparaphenylenediamine, and this, by boiling with acetic anhydride and sodium acetate, was converted into *triacetylparaphenylenediamine*, $C_6H_3Ac(NHAc)_2$, a substance crystallising from hot water in glistening plates melting at 234°. On treatment with dilute sodium hydroxide solution, this yields *diacetohydroxyparaphenylenediamide*, $OH\cdot C_6H_3(NHAc)_2$ $[OH : (NHAc)_2 = 1 : 2 : 5]$, an unstable compound crystallising from hot water in needles melting at 265°; when oxidised with sodium dichromate in acetic acid solution, it gives 2 : 5-*diacetamidoquinone*, $C_6H_2O_2(NHAc)_2$ $[O_2 : (NHAc)_2 = 1 : 4 : 2 ; 5)$. The latter crystallises from glacial acetic acid in straw-coloured needles partly subliming at 300°, and on hydrolysis with sulphuric acid yields 2 : 5-*diamidoquinone* $[O_2 : (NH_2)_2 = 1 : 4 : 2 : 5]$, a violet, crystalline powder melting at 325—330°. On reduction, 2 : 5-diacetamidoquinone yields 2 : 5-*diacetamidoquinol*, $C_6H_3(OH)_2(NHAc)_2$, which is a powder melting at 285—290°; 2 : 5-*diamidoquinol* itself is a white, unstable, crystalline compound, the hydrochloride of which is, however, stable in concentrated hydrochloric acid solution. The *tetracetyl* compound crystallises from glacial acetic acid in glistening needles melting at 190°. That the compound formed by the action of hydroxylamine on dihydroxyquinone does not possess the quinone formula as stated by Nietzki and Schmidt, is shown by its conversion into *sym*-diamidoresorcinol, which, on oxidation, gives amidohydroxyquinoneimide, and on acetylation a *tetracetyl*

compound crystallising from glacial acetic acid in needles melting at 180°, and identical with the compound derived from the diamidoresorcinol obtained from dinitroresorcinol. J. F. T.

Diazotisation of Highly Substituted Anilines, and Formation of the Corresponding Benzonitriles. By ADOLPH CLAUS and REINHOLD WALLBAUM (*J. pr. Chem.*, 1897, [ii], 56, 48—70).—Derivatives of aniline containing several negative groups cannot be diazotised in the usual way. They can be diazotised in large part, however, by dissolving them in sulphuric acid monohydrate, cooling the solution to −10 to −15°, and adding drop by drop a very concentrated aqueous solution of sodium nitrite (in considerable excess of the theoretical amount), the liquid being stirred vigorously by a mechanical stirrer during the addition, which should last 1—1½ hours; on diluting the solution, the unaltered amine is often precipitated, and can be removed by filtration. Fuming 40 per cent. hydrochloric acid can sometimes be used instead of sulphuric acid. Many of these diazo-solutions react but little, or very imperfectly, with sodium naphtholsulphonate to form azo-dyes; yet, even when they give no other of the ordinary diazo-reactions, they are found to yield cyanides by Sandmeyer's reaction. These cyanides, containing several negative groups, it has not yet been found possible to hydrolyse to the corresponding benzoic acid derivatives. In conclusion, it is pointed out that these highly substituted diazo-compounds do not appear to form sulphites, but yield sulphonates immediately; one of the authors (Claus) reiterates his opinion that diazo-sulphites and sulphonates are structurally, and not merely stereochemically, isomeric.

2 : 3 : 4 : 6-*Tetrabromobenzonitrile* was prepared from the corresponding tetrabromaniline, by the diazo-reaction; but it melts at 123°; but after sublimation, at 102°. 2 : 3 : 4 : 5-*Tetrabromaniline* was prepared by nitrating the acetyl derivative of 3-bromaniline; then treating the mixture of 4- and 6-nitro-derivatives with bromine (2 mols.) in acetic acid solution; diazotising the mixture of 2 : 3 : 6-tribromo-4-nitro- and 2 : 3 : 4-tribromo-6-nitro-aniline, and displacing the diazo-group by bromine, by which means a single product, 1 : 2 : 3 : 4-tetrabromo-6-nitrobenzene, melting at 107°, was obtained, finally reducing the last-named substance with stannous chloride. It melts at 122°; the 2 : 3 : 4 : 5-*benzonitrile* obtained from it at 124°. 2 : 3 : 6-*Tribromo-4-nitraniline* (see above) is yellow, and melts at 131°. 1 : 2 : 4-Tribromo-6-nitrobenzene can be obtained by the diazo-reaction from 2 : 4-dibromo-6-nitraniline; it melts at 81° (*not* 119°, Körner), and, when reduced with stannous chloride, yields 2 : 3 : 5-*tribromaniline*, melting at 91°. 2 : 6-Dibromo-4-nitraniline yields 1 : 2 : 6-tribromo-4-nitrobenzene by the diazo-reaction. 2 : 3 : 5 : 6-Tetrabromaniline (Abstr., 1895, i, 345) can be diazotised by the new method; the solution seems to yield a phenol melting at 246°; it will yield also a mixture of pentabromobenzene with perbromobenzene; 2 : 3 : 5 : 6-*tetrabromobenzonitrile* melts at 124°. The three tetrachloranilines can also be diazotised, the 2 : 3 : 5 : 6 isomeride most easily, then the 2 : 3 : 4 : 5, and least easily the 2 : 3 : 4 : 6 isomeride; the derived *tetrachlorobenzonitriles* melt respectively at 72°, 84, and 81°. C. F. B.

Molecular Change of Brominated Diazonium Chlorides into Chlorinated Diazonium Bromides. By ARTHUR R. HANTZSCH, in conjunction with A. SCHLEISSING and M. JÄGER (*Ber.*, 1897, **30**, 2334—2355. Compare Abstr., 1897, i, 408).—Many brominated diazonium chlorides undergo a molecular change, both in the dry state and in solution, by which they pass into chlorinated diazonium bromides. The change of the solid salt is generally accompanied by a partial decomposition of the substance, but in solution no decomposition occurs. The conversion of the chloride into bromide is much more rapid in alcoholic than in aqueous solutions, and is also favoured by concentration and acidity. Compounds containing only one bromine atom do not appear to undergo this remarkable molecular rearrangement, but those in which two atoms are present in ortho- or para-positions relatively to the diazonium group readily change, whilst those with three atoms of bromine react still more rapidly. No instance of the inverse change has yet been observed.

An analogous behaviour is exhibited by the halogen derivatives of the diazonium thiocyanates, which change in a similar manner into thiocyano-diazonium salts.

2 : 4-*Dibromodiazonium chloride*, $C_6H_3Br_2\cdot N_2\cdot Cl$, crystallises with $1H_2O$ in colourless needles, and only changes very slowly in the solid state or in aqueous solution; in alcoholic solution, however, it rapidly passes into 2 : 4-*chlorobromodiazonium bromide*, $C_6H_3ClBr\cdot N_2\cdot Br$, which is a yellow, crystalline powder. When the alcoholic solution of the dibromochloride is saturated with hydrogen chloride, *dichlorodiazonium bromide*, $C_6H_3Cl_2\cdot N_2\cdot Br$, is produced as a microcrystalline powder. 2 : 4-*Dibromorthotoluenediazonium chloride* forms a *hydrochloride*, $3(C_6H_2Br_2Me\cdot N_2\cdot Cl) + HCl$, which crystallises in readily soluble, colourless needles. The diazonium salt only changes slowly and imperfectly into the corresponding chlorobromo- and dichloro-derivative. When, however, it is treated in alcoholic solution with hydrogen chloride, 2 : 4-dichlorotoluene, melting at 26·5°, is formed. 2 : 6-*Dibromoparatoluenediazonium chloride* closely resembles the ortho-compound, but changes rather more rapidly. When treated in alcoholic solution with hydrogen chloride, 2 : 6-dichlorotoluene is formed along with chlorobromotoluene. The 2 : 6-dihalogen toluenediazonium salts occur in two modifications; thus, for instance, dibromotoluenediazonium bromide is obtained in yellow crystals when the alcoholic solution in which the base has been diazotised is immediately treated with ether, whilst, if it be allowed to stand for some time, ether precipitates the salt in brown crystals. These two forms have the same composition, and both explode at 97—98°. The brown salt becomes yellow when exposed to light, and the yellow salt is obtained when ether is added to the alcoholic solution of the brown salt. 3 : 5-*Dibromodiazonium chloride hydrochloride*, $C_6H_3Br_2\cdot N_2\cdot Cl,HCl + 4H_2O$, is obtained by diazotising metadibromaniline. When allowed to stand over potash, it passes into the *salt*, $3(C_6H_3Br_2\cdot N_2\cdot Cl),HCl$, whilst the *normal diazonium salt* is precipitated by the addition of ether to the alcoholic solution. It does not undergo any molecular change into a bromide.

Tribromodiazonium chloride hydrochloride has previously been described. The *salt*, $3(C_6H_2Br_3\cdot N_2\cdot Cl),HCl$, is obtained when the base

is diazotised in solution in acetic acid, or in absolute alcohol at $-5°$. The normal diazonium salt could not be prepared. The monacid salt changes into a bromide with moderate rapidity, even in the solid state, whilst in aqueous solution the change proceeds at a somewhat slower rate; in alcoholic solution, on the other hand, it proceeds with such rapidity that it is impossible to obtain a precipitate of pure silver chloride by adding silver nitrate to a freshly made solution of the salt. It was found extremely difficult to isolate the actual products formed by this molecular change, but they were all recognised by conversion into the corresponding halogen toluene derivatives. In this way, *symmetrical dibromochlorobenzene*, melting at 96°, symmetrical dichlorobromobenzene, and symmetrical trichlorobenzene were all obtained. When the monacid tribromodiazonium chloride hydrochloride is suspended in ether, it becomes yellow, but becomes white again as soon as the ether is removed; this behaviour was repeated a second time on similar treatment, but did not occur when the treatment was repeated a third time. The white salt appears to be *chlorodibromodiazonium chloride*, $C_6H_2ClBr_2{\cdot}N_2{\cdot}Cl$.

Tribromaniline hydrochloride does not undergo any molecular change, so that the reaction appears to be limited to the diazonium salts.

A number of double salts derived from diazonium salts were also examined, but were not found to undergo any similar change. *Tribromodiazonium iodide cadmioiodide*, $C_6H_2Br_3{\cdot}N_2{\cdot}I,CdI_2$, is a dark red salt which becomes yellow and then rapidly decomposes; a second *salt*, $(C_6H_2Br_3{\cdot}N_2{\cdot}I_2),CdI_2$, is even less stable. *Trichlorodiazonium chloride dibromide*, $C_6H_2Cl_3{\cdot}N_2{\cdot}Cl,Br_2$, is a yellow, crystalline mass melting at 136°. *Trichlorodiazonium chloride di-iodide*,

$$C_6H_2Cl_3{\cdot}N_2{\cdot}Cl,I_2,$$

forms reddish-brown crystals which decompose on exposure to light, forming *trichloriodobenzene*, melting at 54°, and *trichlorodiazonium iodide dichloride*, which crystallises in light yellow prisms melting at 156°. *Trichlorodiazonium chloride bromide iodide*, $C_6H_2Cl_3{\cdot}N_2{\cdot}Cl,Br,I$, is formed in orange-red crystals melting at 132°, when the chloride is treated in alcoholic solution with iodine bromide.

Hexachlorodiazoamidobenzene, prepared by the diazotisation of trichloraniline, crystallises in very small, white needles, which decompose at 141°. *Hexabromodiazoamidotoluene* is a white, spongy mass.

A. H.

Alphyl- and Alkyl-Hydroxylamines. By EUGEN BAMBERGER and EDMOND RENAULD (*Ber.*, 1897, 30, 2278—2289).—Azoxy-compounds can be readily obtained by the action of nitrosobenzene on β-alphylhydroxylamines. The authors have obtained theoretical yields of the following: metazoxytoluene (37°), parazoxytoluene (69°), paradichlorazoxybenzene (154°), metadibromazoxybenzene (109—110°), and paradibromazoxybenzene (169—170°). Nitroso- and hydroxylamine compounds which contain different alphyl groups yield a mixture of the two simple azoxy-derivatives, for example, $NO{\cdot}Ph$ and $C_6H_4Me{\cdot}NH{\cdot}OH$ give $Ph{\cdot}N_2O{\cdot}Ph$ and $C_6H_4Me{\cdot}N_2O{\cdot}C_6H_4Me$.

Alkylated hydroxylamines, for example β-benzylhydroxylamine,

react in a different manner, and yield substances polymeric with the azoxy-compounds.

Bisazoxybenzyl, $[(CH_2Ph)_2N_2O]_2$, probably

$$O\langle\begin{matrix}N(CH_2Ph)\cdot N(CH_2Ph)\\N(CH_2Ph)\cdot N(CH_2Ph)\end{matrix}\rangle O,$$

is obtained when pure β-benzylhydroxylamine (7·3 grams) is gradually added to a cooled solution of nitrosobenzene (9·5 grams) in absolute alcohol. It crystallises from boiling xylene in nodular groups of needles melting at 210—211°, and is but sparingly soluble in boiling alcohol or ether. α-Naphthylamine, added to a cold acetic acid solution of the compound, gives an intense violet-red coloration. The compound yields an orange-red colour when added to heated phenol, but does not give Liebermann's reaction. Other products are formed in addition to bisazoxybenzyl by the action of nitrosobenzene on benzylhydroxylamine; among these are azoxybenzene, azobenzene, aniline, benzaldehyde, crystals melting at 200—202°, others at 160° and a red oil.

Phenylazohydroxymethylamide,* $PhN_2\cdot NMe\cdot OH$, is formed when a sodium acetate solution of diazobenzene chloride is slowly added to an acetic acid solution of β-methylhydroxylamine at 0·5° (compare Abstr., 1896, i, 222). It is readily soluble in the usual solvents, with the exception of light petroleum, crystallising from the latter in white, glistening needles melting at 69—70°. With alcoholic copper acetate, it yields a brownish-red precipitate of the normal copper derivative $(N_2Ph\cdot NMeO)_2Cu$, which, after recrystallisation from boiling alcohol, forms dark, brownish-red needles possessing a bronzy lustre. When allowed to crystallise slowly, it forms glistening black prisms of high specific gravity. The azohydroxamide is readily hydrolysed by mineral acids.

Paranitrophenylazohydroxymethylamide, $NO_2\cdot C_6H_4\cdot N_2\cdot NMe\cdot OH$, crystallises from boiling alcohol in glistening, yellow needles, and melts at 231°. It is only sparingly soluble in cold benzene, chloroform, or alcohol, but dissolves in alkalis, giving deep-red solutions.

Paranitrophenylazomethoxymethylamide, $NO_2\cdot C_6H_4\cdot N_2\cdot NMe\cdot OMe$, obtained by the action of alcohol and methylic iodide on the previous compound, crystallises from light petroleum in glistening, brownish-yellow needles melting at 142°.

Paranitrophenylazohydroxybenzylamide crystallises in golden-yellow plates with a bronzy lustre. It melts at 181—182°, and is readily soluble in benzene. *Phenylazohydroxybenzylamide* forms needles melting at 105°; *paratolylazohydroxybenzylamide*, $C_6H_4Me\cdot N_2\cdot N(OH)\cdot CH_2Ph$, crystallises in long, silky needles melting at 106·5°. *Paranitrophenylazo-β-hydroxyamidopropionic acid*, $NO_2\cdot C_6H_4\cdot N_2\cdot N(OH)\cdot CH_2\cdot CH_2\cdot COOH$, crystallises in small, brownish-red needles melting at 177—178°. All these compounds yield characteristic copper derivatives.

α-Benzylhydroxylamine reacts with paranitrodiazobenzene acetate, yielding paranitrodiazobenzoimide, $NO_2\cdot C_6H_4\cdot N_3$ (m. p. 71°), benzylic alcohol, and water. Orthonitrodiazobenzoimide (52°) and orthonitroparadiazotoluoimide (69°) were obtained in a similar manner.

J. J. S.

* The author uses the expression azoamide in place of the usual nomenclature diazoamido-compound; Hantzsch has suggested diazoamide.

N-Alkylhydroxylamines. By ERNST O. BECKMANN (*J. pr. Chem.*, 1897, [ii], 56, 71—93).—When a β-hydroxylamine, NHR·OH, is treated with phenylcarbimide, NPh:CO, in benzene solution, the product is NHPh·CO·NR·OH, and, when heated with a chloride RCl in the presence of alcoholic sodium ethoxide, it yields the compound NHPh·CO·NR·OR. That this is the mechanism of the reaction is evident from the fact that the same final product is obtained starting with the α-hydroxylamine, the intermediate product being different: NH_2·OR→NHPh·CO·NH·OR→NHPh·CO·NR·OR. This final product is, moreover, different from the isomeric compound, NR_2·O·CO·NHPh, obtained by treating the di-β-hydroxylamine, NR_2·OH, with phenylic isocyanate.

Compounds of the type NHPhCO·NR·OBz, when heated, frequently undergo a molecular transformation into others of the type NRBz·O·CO·NHPh. Thiocarbimides also add themselves on to β-hydroxylamines, but under certain circumstances the product is a thiocarbamide, oxygen being lost.—The presence of an OH group in these hydroxylamine derivatives conditions their solubility in alkalis, and a colour reaction with ferric chloride. The following is a list of the compounds described (the numbers quoted are melting points).

[With B. GOETZE.]—*N-Benzylformaldoxime*, 116°; *N-benzylpropionaldoxime*, 106°; *N-benzyloenanthaldoxime*, 85°; $CH_2Ph \cdot N {<}^{O}_{CHR}$.

[With F. SCHÖNERMARK.] — *β-Carbanilido-β-benzylhydroxylamine*, NHPh·CO·N(CH_2Ph)·OH, 163°; its *methylic*, 87°; *ethylic*, 74°; *benzylic*, 107°; *benzoyl*, 120°, and *phenylsulphonic*, 120°, derivatives, NHPh·CO·N(CH_2Ph)·OR. *α-Carbanilido-β-dibenzylhydroxylamine*, $N(CH_2Ph)_2$·O·CO·NHPh, 117°. *α-Carbanilido-β-benzoyl-β-benzylhydroxylamine*, NBz(CH_2Ph)·O·CO·NHPh, 140°.

[With HEINRICH KÖNIG]—*β-Anisylhydroxylamine*, OMe·C_7H_6·NH·OH, 76°; its hydrochloride, 167°; its *β-carbanilido*-derivative,

NHPh·CO·N(C_7H_6·OMe)·OH,

161°; and its *methylic*, 103°; *ethylic*, 92°; *benzylic*, 85°; and *benzoyl*, 134°, derivatives. *α-Carbanilido-β-benzoyl-β-anisylhydroxylamine*,

NBz(C_7H_6·OMe)·O·CO·NHPh,

92°; *$\alpha\beta$-dibenzoyl-β-anisylhydroxylamine*, NBz(C_7H_6·OMe)·OBz, 64°.

[With F. SCHÖNERMARK.]—*β-Carbanilido-β-phenylhydroxylamine*, NHPh·CO·NPh·OH, 125°; and its *methylic*, 74°; and *benzoyl*, 100°, derivatives. *α-Carbanilido-β-benzoyl-β-phenylhydroxylamine*,

NPhBz·O·CO·NHPh,

127°. *α-Benzoyl-β-phenylhydroxylamine*, NPhBz·OH, 120—121°; *$\alpha\beta$-dibenzoyl-β-phenylhydroxylamine*, NPhBz·OBz, 118—119°. *β-Thiocarbanilido-β-benzylhydroxylamine*, NHPh·CS·N(CH_2Ph)·OH, 131—132°. *Thiocarbanilido*, 111°; *thiocarballylamido-*, 98°; and *thiocarbomethylamido-*, 146°; *β-phenylhydroxylamines*, NHPh·CS·NR·OH.

C. F. B.

Nitro-substituted Hydroxamic Acids. By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1897, 16, 184—188).—Paranitrobenzoic chloride reacts with benzhydroxamic acid, yielding paranitrobenzoylbenz-

hydroxamic acid, a compound identical with that obtained by the action of nitrobenzoic chloride on the sodium derivative of phenylnitromethane. Benzoic chloride and paranitrobenzhydroxamic acid yield benzoylparanitrobenzhydroxamic acid, which is identical with the product obtained by the action of benzoic chloride on the potassium derivative of paranitrophenylnitromethane (compare Abstr., 1897, i, 409).

A mixture of *nitrobenzhydroxamic acid* and *dinitrodibenzhydroxamic acid* is obtained by the action of paranitrobenzoic chloride on hydroxylamine; the two may be separated by the action of sodium carbonate solution, which dissolves the mononitro-acid only. The dinitro-acid crystallises from alcohol in pale yellow plates decomposing at 174°; it dissolves slowly in potassium hydroxide solution, and when its alkaline solution is boiled paranitraniline is formed. The mononitro-acid is best obtained by dissolving in glacial acetic acid and adding benzene; it decomposes at 171° and dissolves readily in potassium hydroxide. J. J. S.

Bismarck-brown. By Ernst Täuber and Franz Walder. (*Ber.*, 1897, **30**, 2111—2117).—When Bismarck-brown is prepared by the action of sodium nitrite on metaphenylenediamine dihydrochloride, nitrogen is evolved. When the monhydrochloride is employed, on the other hand, the reaction is not complete, although no gas is evolved. Finally, when 4 molecules of acid are used for 2 of the base, the latter is completely converted into colouring matter, without the evolution of gas. In no case is triamidoazobenzene the sole product, whilst many samples of Bismarck-brown, prepared in the laboratory and also on the large scale, do not contain any of the triamido-compound. Pure triamidoazobenzene is best prepared from its *monacetyl* derivative, which is obtained by diazotising monacetometaphenylenediamine and bringing the resulting salt into reaction with metaphenylenediamine. It forms brick-red, lustrous plates melting at 165°, and when hydrolysed yields triamidoazobenzene, which crystallises with $\frac{1}{2}$ mol. of benzene in plates melting at 143—145°. These belong to the monosymmetric system, the constants being $a:b:c = 1{\cdot}1804:1:1{\cdot}7966$; $\beta = 84° 52'$.

Another substance which is contained in many samples of the colouring matter is a *disazo-compound*, the exact constitution of which has not yet been ascertained. It may be extracted from the base of the colouring matter by benzene, from which it crystallises with $\frac{2}{3}$ mol. of benzene and melts at 118°. When recrystallised from a mixture of benzene and phenol, it separates with 1 mol. of phenol, and then melts at 136°. The base has the composition $C_{18}H_{18}N_8$, and is insoluble in water. A. H.

Bismarck-brown. By Richard Möhlau and Ludwig Meyer (*Ber.*, 1897, **30**, 2203—2206).—In order to prove the correctness of Caro and Griess's statement, that the chief product of the action of sodium nitrite on metaphenylenediamine hydrochloride is triamidoazobenzene, the authors prepared this compound by combining diazotised phenyloxamic acid with metaphenylenediamine and hydrolysing the product.

Metaphenylenediamineazophenyloxamic acid,

$$COOH \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(NH_2)_2,$$

separates from its hot, ammoniacal solution in dark red prismatic crystals on adding excess of dilute acetic acid; it decomposes at 189° without melting, and yields triamidoazobenzene on hydrolysis with dilute sulphuric acid. The hydrochloride of triamidoazobenzene contains 2 mols. of hydrochloric acid to 1 mol. of the base, which is in accordance with Caro and Griess's work; further, it appears to crystallise with $1H_2O$. The melting point, 143·5°, is also in agreement with that found by the above investigators, the *triacetyl* compound crystallises from absolute alcohol in yellow needles melting at 264°.

J. F. T.

Some Ketones of the Phloroglucinol Series. (Researches on the Flavone Derivatives. VII.). By PAUL FRIEDLÄNDER and LUDWIG C. SCHNELL (*Ber.*, 1897, **30**, 2150—2155. Compare Abstr., 1897, i, 442, 482.).—The authors carried out the following experiments with the hope of preparing symmetrical trihydroxyacetophenone from which flavone derivatives might be obtained of a character similar to those which occur in nature. Trimethylphloroglucinol is best obtained by the distillation of the residues of coto bark with caustic soda, after treating them with methylic iodide and an alkali. Trimethylphloroglucinol is converted by acetic chloride, in the presence of aluminium chloride, into di- and tri-methylphloroacetophenone. *Dimethylphloroacetophenone*, $OH \cdot C_6H_2(OMe)_2Ac$, which is the chief product when the residue first obtained is heated with aluminium chloride, crystallises in slender needles, melting at 85—88°. *Trimethylphloroacetophenone* crystallises in almost colourless, striated prisms melting at 97—98°. *Dimethylphloroacetophenone chloride* (dimethoxyhydroxyphenacyl chloride),

$$OH \cdot C_6H_2(OMe)_2 \cdot CO \cdot CH_2Cl,$$

is obtained by heating trimethylphloroglucinol with chloracetic chloride and aluminium chloride, the residue which is formed being finally heated with an excess of aluminium chloride; it crystallises in slender, colourless needles melting at 142—144°, and in alcoholic solution is coloured an intense violet by ferric chloride. *Dimethoxyketocoumaran*, $C_6H_2(OMe)_2<^{O}_{CO}>CH_2$, obtained by warming the foregoing compound, in a fine state of division, with sodium carbonate for a very short time, crystallises in colourless needles melting at 136—138°. Both the acetophenone chloride and the ketocoumaran readily condense with aldehydes. Benzaldehyde yields a substance of the composition of a *dimethylchrysin*, $C_{15}H_8O_2(OMe)_2$, which crystallises in almost colourless needles melting at 150—152°, but is not identical with the compound obtained by Picard by the methylation of monomethylchrysin. Piperonal yields a *compound*, which separates from alcohol in small, yellow crystals melting at 220—224°. Furfuraldehyde also yields a condensation *product*, which crystallises in yellow glistening needles melting at 177—179°. The *compound* formed with protocatechuic aldehyde colours alumina mordants orange-yellow, and chrome mordants yellowish-brown, the shades being markedly more yellow than those produced by the product obtained from the unsubstituted ketocoumaran and the same aldehyde.

A. H.

Paramidobenzaldehyde. By REINHOLD WALTHER and O. KAUSCH (*J. pr. Chem.*, 1897, [ii] 56, 97—123).—*Paramidobenzylidenephenylhydrazone*, $NH_2 \cdot C_6H_4 \cdot CH{:}N \cdot NHPh$, prepared by the action of phenylhydrazine on paramidobenzaldehyde in acetic acid solution, crystallises from alcohol in glistening, yellow leaflets melting at 175°. It is insoluble in water and light petroleum, but soluble in mineral acids, alcohol, and benzene. The *monacetyl* derivative crystallises in yellow leaflets melting at 155°, the *diacetyl* derivative in yellow needles melting at 211°; and the *benzoyl* derivative in yellow leaflets melting at 159—160°.

Aromatic aldehydes react with paramidobenzylidenephenylhydrazone with elimination of water, giving rise to compounds containing the complex $-CH{:}N-$ twice: *benzylideneparamidobenzylidenephenylhydrazone* crystallises from benzene in yellow, microscopic needles melting at 140°, and *orthohydroxybenzylideneparamidobenzylidenephenylhydrazone* in beautiful, yellow, glistening leaflets melting at 173—174°. The hydrazone also reacts with the thiocarbimides; in the case of phenylthiocarbimide, *parabenzylidenephenylhydrazonethiocarbanil* is produced which separates from alcohol in yellow, microscopic crystals melting at 220—221°; allylthiocarbimide gives *parabenzylidenephenylhydrazoneallylthiocarbamide* crystallising from alcohol in yellowish-white leaflets melting at 136°.

When paramidobenzylidenephenylhydrazone is heated in sealed tubes with carbon bisulphide, a compound is formed which crystallises in yellow needles and melts at 220°; it appears to be *dibenzylidenephenylhydrazonethiocarbamide*, $SC(NH \cdot C_6H_4 \cdot CH{:}N \cdot NHPh)_2$.

The action of ethylic acetoacetate on paramidobenzylidenephenylhydrazone was investigated, but the results were unsatisfactory, mainly owing to the insolubility of the substances formed.

Paramidobenzylideneaniline, $NH_2 \cdot C_6H_4 \cdot CH{:}NPh$, may be obtained either by the action of aniline or aniline hydrochloride on paramidobenzaldehyde. It separates from alcohol in yellow leaflets and from ether in yellow needles melting at 110°. It is insoluble in alkalis, but dissolves in acids, and on boiling with them is decomposed into its components. When acted on by carbon bisulphide, a yellowish-green substance is produced which could not be further investigated on account of its insolubility in all menstrua.

Paramidobenzaldoxime, $NH_2 \cdot C_6H_4 \cdot CH{:}N \cdot OH$, prepared by the action of hydroxylamine hydrochloride on paramidobenzaldehyde, separates from hot water in yellow crystals melting at 124°.

Diparamidodibenzylidenehydrazone, $N_2({:}CH \cdot C_6H_4 \cdot NH_2)_2$, obtained when hydrazine sulphate is gradually added to paramidobenzaldehyde, crystallises from alcohol in yellow leaflets melting at 245°.

Paramidobenzylidenediparamidoazobenzene,

$$NH_2 \cdot C_6H_4 \cdot CH(NH \cdot C_6H_4 \cdot N{:}NPh)_2,$$

is obtained by the interaction of paramidoazobenzene and paramidobenzaldehyde. It crystallises from dilute alcohol in red needles melting at 115°, and dissolves in acids with a red coloration. When reduced with zinc dust and acetic acid in alcoholic solution, it is converted into the insoluble modification of paramidobenzaldehyde, aniline, and paraphenylenediamine being also produced.

Diazoamidobenzaldehyde, $COH \cdot C_6H_4 \cdot N{:}N \cdot NH \cdot C_6H_4 \cdot COH$, obtained

by the action of sodium nitrite (1 mol.) on paramidobenzaldehyde (2 mols.) in acetic acid solution, crystallises from light petroleum in golden-yellow leaflets melting at 135°. It may be converted into the corresponding amidoazo-compound.

Diazobenzaldehyde may be prepared by the ordinary method; it was not isolated, but proved to exist in the solution, for, on boiling, nitroparahydroxybenzaldehyde was obtained. Diazobenzaldehyde reacts with amines; the *aniline* compound crystallises from alcohol in yellow leaflets melting at 157°, the *paratoluidine* compound in reddish-brown leaflets melting at 145°, and the *paraphenylenediamine* compound in violet leaflets having no definite melting point. The last named is soluble in sulphuric acid with a beautiful blue-violet coloration, and in hydrochloric acid giving a rose-red solution, but is insoluble in benzene, chloroform, acetone, and water.

Parahydroxybenzeneazobenzaldehyde, $COH\cdot C_6H_4\cdot N\colon N\cdot C_6H_4\cdot OH$, formed by the action of phenol on a solution of diazobenzaldehyde, crystallises from alcohol in glistening red leaflets melting at 195°; it dissolves in alkalis giving a carmine-red solution, whilst with sulphuric acid a dark, orange coloured solution is produced. *Dihydroxybenzeneazobenzaldehyde*, $COH\cdot C_6H_4N\colon N\cdot C_6H_3(OH)_2$. $[(OH)_2 = 1:3]$, prepared from resorcinol and diazobenzaldehyde, forms red crystals which do not melt at 300°.

Diazobenzaldehyde also combines with salicylic aldehyde to form a substance crystallising in yellow leaflets melting at 180°. A. W. C.

Action of Diacetonitrile on Aldehydes. By ERNST MOHR (*J. pr. Chem.*, 1897, **56**, 124—142).—*Benzylidenediamidocrotononitrile* or *benzylidenedi-imidoacetacetonitrile*, $CHPh[C(CN)\colon CMe\cdot NH_2]_2$ or $CHPh[CH(CN)\cdot CMe\colon NH]_2$. When benzaldehyde is acted on by diacetonitrile, a substance of the composition $C_{15}H_{16}N$ is produced. The author has not been able to decide which of the above constitutional formulæ it possesses, but hopes shortly to satisfactorily prove this point. The same remark applies to the condensation products of diacetonitrile with other aldehydes, mentioned in this abstract. The compound crystallises from absolute alcohol in prisms melting at 190° with partial decomposition and evolution of gas. It is almost insoluble in benzene and ether, but readily soluble in water and absolute alcohol.

3 : 5-*Dicyano*-4-*phenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*,

$$NH{<}\begin{matrix}CMe\colon C(CN)\\ CMe\colon C(CN)\end{matrix}{>}NPh,$$

is produced with elimination of ammonia when benzylidenediamidocrotononitrile is treated with concentrated hydrochloric acid, acetic anhydride, or sulphuric acid. It separates from alcohol as a yellowish, crystalline powder melting at 204—206°. It remains unchanged after heating at 105° for some hours, is easily soluble in acetic acid and caustic soda, and sparingly in dilute hydrochloric or sulphuric acids; it is remarkable that the solution in hot hydrochloric acid or sodium hydroxide is deep yellow, and on cooling, the substance crystallises out, leaving the mother liquor colourless.

Paramethoxybenzylidenediamidocrotononitrile or *paramethoxybenzyli-*

denedi-imidoacetoacetonitrile, $OMe\cdot C_6H_4\cdot CH[C(CN):CMe\cdot NH_2]_2$ or $OMe\cdot C_6H_4\cdot CH[CH(CN)\cdot CMe:NH]_2$, is obtained when anisaldehyde is gradually added to diacetonitrile suspended in benzene. It crystallises from water in snow-white prisms, and from alcohol in long needles sparingly soluble in benzene or ether. When quickly heated, it melts at 188—192°, but on slowly heating, the greater portion melts at 155—160°; in this case, it becomes yellow, and between 175 and 180° evolves gas.

3 : 5-*Dicyano*-4-*paramethoxyphenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*, $OMe\cdot C_6H_4\cdot CH<\begin{matrix}C(CN):CMe\\C(CN):CMe\end{matrix}>NH$, is obtained in snow-white needles melting at 215—216°, when acetic anhydride acts on paramethoxybenzylidenediamidocrotononitrile. It is soluble in alcohol and chloroform, but only sparingly so in ether, benzene, and light petroleum.

Metanitrobenzylidenediamidocrotononitrile (*metanitrobenzylideneacetoacetonitrile*) crystallises from alcohol in yellow, transparent prisms melting at 118—120°; the corresponding *piperonylidene* compound separates from alcohol in needles melting at 210°; and the *cinnamylidene* compound in compact prisms melting at 149—159°; the latter is coloured red on exposure to air.

The condensation of salicylaldehyde with diacetonitrile takes place in two ways, as represented by the following equations,

I. $HO\cdot C_6H_4\cdot CHO + 2C_4H_6N_2 = H_2O + NH_3 + C_{15}H_{13}N_3O$.
II. $2HO\cdot C_6H_4\cdot CHO + C_4H_6N_2 = 2H_2O + C_{18}H_{14}N_2O_2$.

The compound produced according to reaction I is,

3 : 5-*Dicyano*-4-*orthohydroxyphenyl*-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*; it crystallises from absolute alcohol in colourless, glistening, transparent four-sided prisms. When heated to 230—240°, it turns yellow, and melts between 265—270°, becoming black.

The compound $C_{18}H_{14}N_2O_2$ crystallises from alcohol in colourless needles melting at 179—180°, but the author has been unable to decide its constitution. When treated with acetic anhydride, ammonia is not eliminated, but a *monacetyl* derivative is produced crystallising from a mixture of dry benzene and light petroleum and melting at 170°. It is very unstable, readily giving up the acetyl group, the original substance being regenerated.

When the compound $C_{18}H_{14}N_2O_2$, in glacial acetic acid solution, is boiled with hydrochloric acid, a *polyacetyl* derivative is obtained crystallising from glacial acetic acid in colourless needles melting at 209—211°; like the monacetyl derivative, it is very unstable.

A. W. C.

Action of Benzaldehyde on Ketones. By DANIEL VORLÄNDER (*Ber.*, 1897, 30, 2261—2268. Compare Abstr., 1896, i, 546 and 603, Petrenko-Kritschenko, *ibid.*, i, 472). Dipropyl ketone (40 grams), benzaldehyde (37 grams), alcohol (300 c.c.), water (200 c.c.) and 10 per cent. sodium hydroxide solution (40 c.c.) are mixed together and allowed to stand in a stoppered vessel for some 30 days, care being taken that the mixture is well shaken from time to time. The oil which is obtained when the ether is distilled from the ethereal extract is subjected to distillation under a pressure of 40 mm., when the

following fractions are obtained: 100—107°, about 14·8 grams, consisting mainly of benzaldehyde; 150—170°, 4 grams; 170—190°, about 13·7 grams, consisting mainly of *benzylidenedipropyl ketone*, $CHPh\colon CEt\cdot CO\cdot CH_2Et$, and 200—235°, about 8 grams of a syrupy oil consisting of *diphenyldiethylhydropyrone*, $CO<\begin{matrix}CHEt\cdot CHPh\\CHEt\cdot CHPh\end{matrix}>O$.

No better yield of these two compounds can be obtained by using 2 mols. of benzaldehyde to 1 of the ketone. The author attributes the poor yield, as compared with the corresponding reaction between benzaldehyde and diethyl ketone, to stereochemical influences. Benzylidenedipropyl ketone is a colourless oil distilling at 176—178° under a pressure of 40 mm.; it is readily miscible with alcohol or ether and alcohol, and reacts with methylic malonate in the presence of a small quantity of sodium methoxide, yielding *methylic phenyldiethylhydroresorcylate*, $CO<\begin{matrix}CHEt—CO\\CHEt\cdot CHPh\end{matrix}>CH\cdot COOMe$, which crystallises in prisms melting at 139°. The yield is good. *Phenyldimethylhydroresorcylic acid*, obtained by allowing its methylic salt (Abstr., 1896, i, 546) to remain in contact with an excess of aqueous alcoholic potash for 10 days, crystallises in colourless crystals; it melts at 124°, and is at the same time converted into *phenyldimethylhydroresorcinol*. This melts at 190—192° to a yellow liquid, and gives a brownish coloration with ferric chloride.

Benzaldehyde reacts with an aqueous alcoholic solution of suberone in the presence of sodium or potassium hydroxide, the only product being Wallach's dibenzylidenesuberone (Abstr., 1896, i, 572); this readily combines with 4 atoms of bromine, yielding an *additive* compound which melts and decomposes at 185°.

Benzaldehyde does not react with pinacone under the conditions given above. It is stated that pinacone is not transformed into pinacolin by boiling with concentrated sodium carbonate, or by heating with water at 120—130°. The transformation, however, can easily be accomplished by boiling with a 5 per cent. oxalic acid solution for 12 hours, or by boiling for 3—4 hours with a 50 per cent. solution of tartaric, phosphoric, or oxalic acid. Benzaldehyde and methyl propyl ketone yield an oily benzylidene derivative and a complex crystalline compound melting at 197°; the latter is neither a simple dibenzylidene derivative nor yet a hydrophorone. Phorone and mesityloxide both react with benzaldehyde in the presence of sodium hydroxide, yielding complex amorphous compounds. J. J. S.

Benzylidenepinacolin. By Daniel Vorländer and Fritz Kalkow (*Ber.*, 1897, **30**, 2268—2274. Compare preceding abstract).—A theoretical yield of *benzylidenepinacolin*, $CHPh\colon CH\cdot CO\cdot CMe_3$, is obtained when a mixture of benzaldehyde (21·2 grams), pinacolin (20 grams), alcohol (75 c.c.), water (25 c.c.), and 10 per cent. sodium hydroxide solution (20 c.c.) is allowed to stand for 9 days. It crystallises from aqueous alcohol in flat prisms melting at 41°, and is soluble in alcohol, ether, benzene, chloroform, and light petroleum. A *compound*, $C_{13}H_{20}N_2O_2$ (probably benzylidenepinacolinoxime + hydroxylamine), is obtained when an aqueous alcoholic solution of benzylidenepinacolin

(1 mol.) is boiled with hydroxylamine hydrochloride (4—5 mols.) and the requisite quantity of soda for 8 hours. It crystallises in colourless needles, melts at 145—146°, is readily soluble in dilute hydrochloric acid or in sodium hydroxide solution, also in ether, benzene, or chloroform, is almost insoluble in water, and reduces Fehling's solution in the cold. A *δ-ketonic acid*, $COOH\cdot CH_2\cdot CHPh\cdot CH_2\cdot CO\cdot CMe_3$, is obtained by the combination of benzylidenepinacoline with ethylic malonate in the presence of sodium ethoxide and the subsequent elimination of a molecule of carbonic anhydride; it crystallises from boiling water in needles melting at 124°. The *oxime*, $C_{15}H_{21}O_3N$, of the ketonic acid crystallises in flat prisms, melts at 131°, and has an acid reaction. The *amide*, $C_{15}H_{21}O_2N$, obtained by the action of concentrated aqueous ammonia on the acid anhydride, crystallises from boiling water or from benzene in flat needles melting at 133°. Bromine readily reacts with a chloroform solution of benzylidenepinacolin, yielding a *dibromide*, $CHPhBr\cdot CHBr\cdot CO\cdot CMe_3$, which crystallises from boiling alcohol in large prisms melting at 124°. A *β-diketone*, $COPh\cdot CH_2\cdot CO\cdot CMe_3$, and not the acetylene derivative, $CPh⋮C\cdot CO\cdot CMe_3$, is formed by the action of alcoholic potash on the dibromide. It is a colourless oil distilling at 161—165° under a pressure of 25 mm.; when treated with bromine in chloroform solution, it yields a monobromo-derivative, $COPh\cdot CHBr\cdot CO\cdot CMe_3$, crystallising in glistening prisms and melting at 106°. The diketone (3 grams), when heated for 5 hours on the water bath with phenylhydrazine (2 grams) and glacial acetic acid (5 c.c.) yields a *pyrazole* derivative, $CH\Big<{C(CMe_3)\cdot NPh \atop CPh\!=\!=\!N}$ or $CH\Big<{C(CMe_3)⋮N \atop CPh\!=\!=\!NPh}$. This crystallises in colourless prisms, melts at 77°, distils at 229—231° under a pressure of 25 mm., and is insoluble in dilute acids or alkalis. On boiling with concentrated potassium hydroxide, the diketone is decomposed into acetophenone and trimethylacetic acid.

The author considers that his results confirm the usual constitution ascribed to pinacolin, and thinks that but slight importance should be attached to Delacre's criticisms (Abstr., 1896, i, 591, 602), since zinc alkyl syntheses are not always trustworthy. J. J. S.

Derivatives of Paramidophenoxyacetic Acid. By Curtis C. Howard (*Ber.*, 1897, 30, 2103—2107. Compare Abstr., 1897, i, 283).—*The hydrazone of benzylideneparaphenoxyacetic acid*, $C_{15}H_{14}N_2O_3$, formed when benzaldehyde reacts with hydrazidoparaphenoxyacetic acid in alcoholic solution, crystallises from dilute alcohol in greenish-yellow scales melting at 158°, the *tartrazine* dye from hydrazidoparaphenoxyacetic acid is formed when the latter is treated with sodium dihydroxytartrate, and is obtained in orange-red crystals melting at 242°. On heating the hydrazido-acid with ethylic acetoacetate in alcohol solution, *methylpyrazoloneparaphenoxyacetic acid*, $C_{12}H_{12}N_2O_4$, is produced, which crystallises from dilute alcohol in white needles melting at 211°; the *methylic* salt is an oil. *Orthometadinitroparacetamidophenoxyacetic acid*, $NHAc\cdot C_6H_2(NO_2)_2\cdot O\cdot CH_2\cdot COOH$, obtained by the nitration of paracetamidophenoxyacetic acid, crystallises from hot water in yellow crystals melting at 205°, and on reduction gives

the anhydride of *μ-methylmetamidoparaphenoxyacetic acid imidazole*, which crystallises from alcohol in glistening plates melting at 243°. *Orthonitroparamidophenoxyacetic acid*,

$$NH_2{\cdot}C_6H_3(NO_2)O{\cdot}CH_2{\cdot}COOH\ [NH_2:NO_2=2:4],$$

is formed when paramidophenoxyacetic acid in concentrated sulphuric acid solution is treated with the theoretical quantity of potassium nitrate; it crystallises from water in brown prisms melting at 196°, and on reduction gives *orthoparadiamidophenoxyacetic anhydride*, which crystallises from water in thin prisms melting at 225°, the *ethylic* salt melts at 58°. *Paracetamidophenoxyacetic acid paraphenetide*,

$$NHAc{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OEt,$$

from paracetamidophenoxyacetic acid and paraphenetidine, crystallises from dilute acetic acid in microscopic crystals melting at 198°.

J. F. T.

The Nitration of Coumarone. By RICHARD STOERMER and O. RICHTER (*Ber.*, 1897, **30**, 2094—2096).—Coumarone readily reacts with concentrated nitric acid, with the production of two isomeric nitro-derivatives, and also of 5-nitrosalicylic acid. *Paranitrocoumarone*, $C_8H_5O{\cdot}NO_2$, crystallises in yellow, glistening needles melting at 134°, and *orthonitrocoumarone* in yellow needles melting at 85°. The monohalogen derivatives of coumarone likewise yield nitro-derivatives, thus, from bromocoumarone, *nitrobromocoumarone*, $C_8H_4OBr{\cdot}NO_2$, is produced, and from chlorocoumarone, *nitrochlorocoumarone*, $C_8H_4OCl{\cdot}NO_2$, the former separating from dilute alcohol in glistening needles melting at 132°; and the latter in yellow needles melting at 147°. J. F. T.

Action of Hübl's Reagent on Gallic and Tannic Acids. By CARL BOETTINGER (*Chem. Zeit.*, 1896, **20**, 984—985).—Under similar conditions, gallic acid reacts with a larger quantity of the reagent than does tannic acid. With gallic acid, a golden-yellow substance is obtained which is readily soluble in water; with tannic acid, a yellow granular precipitate which is almost insoluble in water. Both substances give up iodine readily. The reaction with both acids takes place much more readily when concentrated solutions of Hübl's reagent are employed. J. J. S.

Production of Acid Ethereal Salts from Acid Anhydrides. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, **18**, 418—432. Compare Abstr., 1895, i, 420).—The author has previously stated the view that, by the action of alcoholic sodium derivatives on the anhydrides of unsymmetrical dibasic acids, ethereal salts are produced different from those formed by the action of alcohol alone. As the only observation of this description made on camphoric anhydride (Bredt, *Annalen*, 1896, **292**, 98) does not agree with this supposition, the author has studied the action of sodium methoxide on hemipinic anhydride. He finds that when this substance is acted on by sodium methoxide in presence of methylic alcohol or benzene, both the α- and β-salts are produced in considerable quantities; the production of the β-salt increases the less alcohol or water is present. In the absence of disturbing secondary reactions, the β-salts form a normal product of the action of alcoholic sodium derivatives on acid anhydrides. The β-methylic salt

of hemipinic acid is not to any considerable extent converted into the α-salt by the action of sodium methoxide.

These facts are to be expected if Ostwald's hypothesis, that chemical reactions take place between ions, be accepted. The ions of sodium methoxide are Na and OCH_3 and of methylic alcohol OH and CH_3: so that if one supposes an anhydride group always splits in the same manner, the following equations will represent the changes which take place.

$$X\begin{matrix}\diagup CO{\cdot}O{\cdot}\ (\alpha)\\ \diagdown CO{\cdot}\quad (\beta)\end{matrix} + \begin{matrix}CH_3\\ OH\end{matrix} = X\begin{matrix}\diagup COOCH_3\ (\alpha)\\ \diagdown COOH\quad (\beta)\end{matrix}$$

$$X\begin{matrix}\diagup CO{\cdot}O{\cdot}\ (\alpha)\\ \diagdown CO{\cdot}\quad (\beta)\end{matrix} + \begin{matrix}Na\\ OCH_3\end{matrix} = X\begin{matrix}\diagup COONa\quad (\alpha)\\ \diagdown COOCH_3\ (\beta)\end{matrix}$$

The author finds that the α-methylic salt of hemipinic acid exists in two stereoisomeric forms, the one melting at 121—122°, and the other at 138°. Details of the work will be given later.

A. W. C.

Intramolecular Rearrangement of Sulphonic Acids. II. By Eugen Bamberger and Jac. Kunz (*Ber.*, 1897, **30**, 2274—2277. Compare Abstr., 1897, i, 286).—The potassium salt of phenylsulphonamic acid is readily transformed into orthamidobenzenesulphonic acid if it is mixed with acetic acid containing a few drops of sulphuric acid and kept at 0° for about 80 hours. The ortho-acid is converted into the isomeric paramidobenzenesulphonic acid when heated with sulphuric acid at 180—190° for 7 hours.

J. J. S.

Condensation with Phenylacetone. By Guido Goldschmiedt and Gustav Knöpfer (*Monatsh.*, 1897, **18**, 437—446).—When the product of the condensation of phenylacetone with benzaldehyde in presence of potassium hydroxide is repeatedly recrystallised from alcohol, two substances are produced, one melting at 71° and the other at 153°.

The substance melting at 71° has the formula $C_{16}H_{14}O$, and must be either *benzyl styryl ketone*, $CH_2Ph{\cdot}CO{\cdot}CH{:}CHPh$, or *stilbyl methyl ketone*, $CH_3{\cdot}CO{\cdot}CPh{\cdot}CHPh$. It is easily soluble in alcohol, ether, and benzene, and on treatment with alkalis appears to be reconverted into its constituents. It reacts with hydroxylamine, yielding a substance melting at 102—103° and easily soluble in alcohol, ether, or benzene, but with difficulty in water. It is insoluble in acids and alkalis, and after boiling with acetic anhydride, the unchanged substance is precipitated by water, pointing to the fact that it is not an oxime, but a substance which has undergone an isomeric change, such a change having been previously noticed in the case of unsaturated ketones (compare Gattermann and Stockhausen, Abstr., 1893, i, 164, and Knoevenagel and Klages, Abstr., 1895, i, 48).

The substance melting at 153° crystallises from alcohol in beautiful, glistening crystals of which the constitution has not yet been definitely decided, but it seems probable that it is *triphenyltetrahydro-γ-pyrone*.

When hydrochloric acid is used as the condensing agent in place of potassium hydroxide, a substance of the composition $C_{16}H_{15}ClO$ is produced, which crystallises in small, colourless needles melting at

140°. When heated at its melting point, hydrogen chloride is given off, and a ketone, $C_{16}H_{14}O$, is formed, which crystallises from alcohol and melts at 53—54°. This ketone is isomeric with the one produced in the condensation with potassium hydroxide, and if in the first case benzyl styryl ketone is produced, this substance must be stilbyl methyl ketone, or *vice versa*, or it may be a stereoisomeride. Further experiments must decide this point.

If sulphuric acid is used for effecting the condensation, the product is a *hydrocarbon* of the formula $C_{27}H_{24}$, probably formed in a similar manner to mesitylene from acetone; it crystallises from alcohol in colourless leaflets melting at 120°. A. W. C.

Furfurobenzidine. By HUGO SCHIFF (*Ber.*, 1897, **30**, 2302—2303).—A claim for priority.

Hydroxybenzylideneindanedione. By STANISLAUS VON KOSTANECKI and L. LACZKOWSKI (*Ber.*, 1897, **30**, 2138—2144).—*Orthohydroxybenzylideneindanedione*, $C_6H_4{<}{\substack{CO\\CO}}{>}C{:}CH{\cdot}C_6H_4{\cdot}OH$, obtained by heating indanedione with salicylaldehyde at 100°, crystallises in rosette-shaped groups of orange-red prisms, which have a violet surface lustre and decompose at 196°. It forms a yellow solution in concentrated sulphuric acid, and is readily decomposed by alkalis. Acetic anhydride converts it into the *acetyl* derivative, which crystallises in rosette-shaped groups of yellow needles melting at 124—125°. *Orthoethoxybenzylideneindanedione*,

$$C_6H_4{:}(CO)_2{:}C{:}CH{\cdot}C_6H_4{\cdot}OEt,$$

can only be prepared by the action of ethylsalicylaldehyde on indanedione. It forms small, yellow crystals melting at 135° and yields a red solution with sulphuric acid. *Metahydroxybenzylideneindanedione* crystallises in yellow plates melting at 222°, and its *acetyl* derivative crystallises in yellowish needles melting at 140°. *Metethoxybenzylideneindanedione* crystallises in yellowish plates melting at 131—132°. *Parahydroxybenzylideneindanedione* separates from acetic acid in lustrous, orange-yellow needles melting at 239°, and its *acetyl* derivative also forms yellow needles which melt at 162°, whilst *parethoxybenzylideneindanedione* crystallises in matted, yellow needles and melts at 139°.

Furfurylideneindanedione, $C_6H_4{:}(CO)_2{:}C{:}CH{\cdot}C_4H_3O$, obtained by the condensation of furfuraldehyde with indanedione, crystallises in lustrous, greenish needles melting at 203°.

Cinnamylideneindanedione, $C_6H_4{:}(CO)_2{:}C{:}CH{\cdot}CH{:}CHPh$, is prepared from cinnamaldehyde, and crystallises in long, orange-coloured needles melting at 150—151°.

When indanedione is heated at 120—125°, the anhydrodi-indanedione which is produced (Wislicenus and Kötzle, Abstr., 1889, 1067) is accompanied by tribenzoylenebenzene, $C_{27}H_{12}O_3$, which was first obtained by Gabriel and Michael (Abstr., 1878, 229). A. H.

Action of Methylic Iodide on Aqueous Solutions of Crystal-Violet, Malachite-Green and Methylene-Blue; Hydrolysis of these Colouring Matters. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1896, [iii], **15**, 1299—1313).—When an aqueous solution of

crystal-violet, $CCl(C_6H_4 \cdot NMe_2)_3$ is mixed with methylic iodide, lustrous, long needles of the corresponding iodine compound gradually separate, and aniline-green and the compound $C(C_6H_4 \cdot NMe_3I)_3 \cdot OH + 3H_2O$ are formed in smaller quantity at the same time, the production of aniline-green being greater the higher the temperature. In dilute solutions (1 part of crystal violet in 800 parts of water), aniline-green is not formed. Detailed investigation of the reaction leads to the following conclusions. In dilute aqueous solutions, methylic iodide acts on the compound $CCl(C_6H_4 \cdot NMe_2)_3$ with formation of the corresponding iodine derivative and methylic chloride. Part of the methylic iodide is hydrolysed and the hydrogen iodide also interacts with the crystal-violet, forming a further quantity of the iodine compound. Part of the violet is also decomposed by water with liberation of hydrochloric acid and formation of the corresponding carbinol, and the latter combines with methylic iodide, yielding the compound $C(C_6H_4 \cdot NMe_3I)_3 \cdot OH$; the methylic chloride formed in the reaction is also partially hydrolysed, and the liberated acid retards the action. The formation of the methiodide is subsequent to the formation of the carbinol.

A dilute aqueous solution of malachite-green, under similar conditions, yields the compound $CPh(C_6H_4 \cdot NMe_2)_2I$ in lustrous crystals, together with methiodides, the reaction being similar to that with crystal-violet. Methylene-blue behaves similarly, and it would seem that the dialkyltriamido-derivatives of triphenylcarbinol unite directly with methylic iodide, which converts them into iodammoniums at the ordinary temperature, even in presence of large quantities of water. The colouring matters in aqueous solution are partly hydrolysed, and when combination with methylic iodide suppresses the basic function, the acid remains free. The author points out that the occurrence of hydrolysis furnishes no definite evidence as to the constitution of the compounds (compare Abstr., 1896, i, 376, 377).

C. H. B.

Di-β-naphthaquinone Oxide. By K. HERMANN WICHELHAUS (*Ber.*, 1897, **30**, 2199—2203).—*Di-β-naphthaquinone oxide*, $O(C_{10}H_5O_2)_2$, which is readily prepared from β-naphthaquinone by oxidation with ferric chloride, crystallises from acetic acid or acetone in slender, orange-yellow needles which melt at 245°, and yields two hydrates on treatment with water, one of which, $C_{20}H_{10}O_5 + 2H_2O$, is red, the other, $C_{20}H_{10}O_5 + 5H_2O$, black; the latter is converted into the former on heating it to 110—120°.

On reducing the freshly precipitated oxide with stannous chloride and hydrochloric acid, it is converted into an unstable compound, which yields an *acetyl* compound probably of the constitution

$$O[C_{10}H_5(OAc)_2]_2,$$

melting at 164—165°; by the action of sulphurous acid a *substance*, $C_{20}H_{14}O_5$, melting at 138° is obtained.

The *oxime of di-β-naphthaquinone oxide* is only slightly soluble in water, the *phenylhydrazone* is brick-red, melts at 264°, and colours wool and silk yellow; the oxide further forms compounds with aniline, dimethylaniline, quinoline and resorcinol, the analyses of which show the correctness of the above formula.

J. F. T.

Azoquinones. By FRIEDRICH KEHRMANN and M. GOLDENBERG (*Ber.*, 1897, **30**, 2125—2130).—2-Hydroxy-α-naphthaquinone readily reacts with diazo-salts to form azo-compounds in which the nitrogen atom occupies the position 3 in the naphthalene ring, and which are converted by reduction into 2-hydroxy-3-amido-α-naphthaquinone and the base corresponding with the diazo-salt employed. These hydroxyazoquinones are brick-red to dark-red in colour and yield crystalline salts with bases, the ammonium salts being specially characteristic. 3-*Benzeneazo-2-hydroxynaphthaquinone*,

$$OH\cdot C_{10}H_4O_2\cdot N_2\cdot Ph,$$

crystallises in fascicular groups of needles melting and decomposing at 225—226°. The *ammonium* salt forms violet-brown, lustrous needles which decompose at 215—217°. The *silver* salt is a black powder. The *oxime*, $OH\cdot C_{10}H_4O(NOH)\cdot N_2\cdot Ph$, is a sulphur-yellow, crystalline powder which forms a blood-red solution in sulphuric acid.

3-*Orthotolueneazo-2-hydroxynaphthaquinone*, $C_{10}H_5O_3\cdot N_2\cdot C_6H_4Me$, crystallises in garnet-red needles, which have a blue, metallic lustre and melt at 205°. The *ammonium* salt forms dark-red, lustrous needles decomposing at 198°, and the *oxime* is an orange-yellow, crystalline powder decomposing at 210—212°. 3-*Paratolueneazo-2-hydroxynaphthaquinone* crystallises in light red needles which melt and decompose at 205°; whilst the *oxime* is a brownish-yellow, crystalline powder which melts and decomposes at 176—178°. 3-*Orthonitrobenzeneazo-2-hydroxynaphthaquinone* crystallises in orange-yellow needles which melt and decompose at 255—257°. 3-*Paranitrobenzeneazo-2-hydroxynaphthaquinone* forms orange coloured plates decomposing at 260—261°.

3-*Parasulphobenzeneazo-2-hydroxynaphthaquinone*,

$$C_{10}H_5O_3\cdot N_2\cdot C_6H_4\cdot SO_3H,$$

forms a *sodium* salt which crystallises in yellowish-red plates. *Parasulphonaphthaleneazohydroxynaphthaquinone*, $C_{10}H_5O_3\cdot N_2\cdot C_{10}H_6SO_3H$, yields a *sodium* salt which crystallises in small, dark-brown, sparingly soluble needles. *β-Naphthaleneazohydroxynaphthaquinone*,

$$C_{10}H_5O_3\cdot N_2\cdot C_{10}H_7,$$

crystallises in garnet-red needles decomposing at 247—248°. A. H.

Methylamide and Dimethylamide of Naphthalene-β-sulphonic Acid. By L. T. C. SCHEY (*Rec. Trav. Chim.*, 1897, **16**, 181—183).—The requisite quantity of standard potassium hydroxide solution is added to 3 grams of methylamine hydrochloride dissolved in a small quantity of water, ether is run in and then 5 grams of naphthalene-β-sulphonic chloride; after vigorously shaking, half the quantity of potash solution previously used, and then $2\frac{1}{2}$ grams of the chloride are added, this process being repeated until 10 grams of chloride have been added to 3 grams of methylamine hydrochloride. The white deposit which separates together with the residue left on evaporating the ethereal solution is recrystallised from alcohol, when the *methylamide* is obtained in a crystalline form melting at 107°. It is sparingly soluble in cold water, ether, or light petroleum, more readily in hot water, and dissolves with extreme ease in absolute alcohol, benzene or chloroform.

Naphthalene-β-sulphondimethylamide, is much more readily soluble in

ether, from which it crystallises in plates melting at 96°. It is not soluble in cold water, but dissolves with great ease in chloroform or benzene. J. J. S.

Constituents of Oil of Roses and Allied Ethereal Oils. By HUGO ERDMANN (*J. pr. Chem.*, 1897, [ii], 56, 1—47) (with ERNST ERDMANN).—*Pure rhodinol*, $C_{10}H_{17}\cdot OH$, was prepared from silver rhodinylic phthalate (see below), itself obtained from commercial geraniol, by treating it with sodium chloride, hydrolysing the resulting sodium salt with alkali, and distilling over the rhodinol with steam; if it is prepared by the hydrolysis of the diphenylurethane, it is difficult to free it from diphenylamine. It boils at 110·5—111° under 16 mm. pressure, and can be boiled under atmospheric pressure, but then undergoes a certain amount of decomposition; it has sp. gr. = 0·8812 at 16°/4°; and it has a most pleasant odour of roses. If a drop is diluted with 5 c.c. of alcohol in a porcelain basin and 10 drops of strong sulphuric acid added, the latter becomes orange-yellow; when the basin is gently swayed, this colour changes to reddish-violet at the surface of separation between the two liquids, and disappears entirely as the liquids mix completely. This may be used as a qualitative test for rhodinol, although both linalool and citronellol give somewhat similar colorations.

Characteristic Derivatives of Rhodinol (with P. HUTH).—Diphenylcarbamic chloride is best obtained by dissolving diphenylamine (100 grams) in chloroform (300 c.c.), and passing in excess of carbonic chloride (40—50 grams). In this way, half of the diphenylamine is recovered as the hydrochloride; by adding pyridine (50 grams), a complete conversion is obtained, pyridine hydrochloride being formed; the carbonic chloride (60 grams) is in this case passed in at 0°. Rhodinylic diphenylurethane, $NPh_2\cdot COOC_{10}H_{17}$ (Abstr., 1896, i, 198) was prepared from crude rhodinol obtained by the acetate method from genuine geranium oil produced at Grasse, in the south of France; it was heated (50 c.c.) with diphenylcarbamic chloride (75 grams) and pyridine (35 c.c.) for 5 hours at 100°, the product being washed with dilute acid, alkaline carbonate and water, freed from impurities by distilling these over with steam, and finally crystallised from alcohol. It melts at 82·2°, and forms a *tetrabromide*, melting when not quite pure at 129—132°, but it also readily takes up 6 other atoms of bromine by substitution, after which it very readily decomposes, yielding hexabromodiphenylamine as one of the products. *Rhodinylic benzoate*, obtained by gradually adding benzoic chloride (20 c.c.) to a mixture of rhodinol (30 c.c.) and pyridine (25 c.c.) kept at 0°, is a colourless oil, and boils at 194—195° under 12 mm. pressure. *Rhodinylic hydrogen phthalate*, $COOH\cdot C_6H_4\cdot COOC_{10}H_{17}$, is obtained by heating rhodinol (10 c.c.) with finely powdered phthalic anhydride (8·6 grams) in the water bath, with constant shaking until solution is just complete, and distilling over impurities with steam; it is a colourless syrup with acid properties, and inflames the mucous membrane when brought in contact with it. The *silver* salt provokes sneezing when inhaled; it melts at 133°; it can be purified by dissolving it in its own weight of benzene and precipitating it with

warm methylic alcohol; it reacts with methylic and ethylic iodides and benzylic chloride in benzene solution, forming *methylic*, *ethylic*, and *benzylic* salts, which are oils that decompose when distilled.

Many of the usual analogies do not hold in the case of rhodinol. It does not react readily with carbamic chlorides other than the diphenyl one; with *paraditolyl-* (melting at 103°) and *α-dinaphthyl-carbamic chlorides* no compound could be obtained, and *phenylbenzylcarbamic chloride* gave a liquid compound of doubtful purity; *β-dinaphthylcarbamic chloride* melting at 151°, does, however, yield a crystallised *rhodinylic urethane* which melts at 105—107°. Further, diphenylcarbamic chloride itself does not react with other alcohols more or less similar to rhodinol; with linalool, terpineol and amylene hydrate, for example, no compound is formed; citronellol, however, forms a liquid diphenylurethane, which does not solidify at 0°. Again, although ethylic bromide reacts but slowly and incompletely with silver rhodinylic phthalate, benzylic chloride reacts quite readily; and although benzylic chloride reacts, paranitrobenzylic chloride does not. Lastly, no other anhydrides of dibasic acids, not even tetrachloro- and tetrabromophthalic anhydrides, react with rhodinol as phthalic anhydride does, yielding a product from which rhodinol can easily be recovered.

Occurrence and Detection of Rhodinol in Ethereal Oils (with P. HUTH).—The possible presence of rhodinol is first recognised by the sulphuric acid test. The oil (1 gram) is then heated in a test-tube with diphenylcarbamic chloride (1·5 grams) and pyridine (1·35 grams) for 2 hours at 100°, and the product is distilled with steam until a litre of distillate has collected, diphenylamine, derived from unchanged carbamic chloride, passing over. The residue, which solidifies on cooling, is recrystallised from 30 times its weight of alcohol; the yield of solid crystalline product is much reduced if citronellol is present, as this forms a liquid urethane. In this way, samples of oil of roses from Turkey and Germany were examined; of geranium oil from France, Bourbon (Réunion) and Syria; oil of ginger-grass; of citronella; of palmarosa from Turkey, and of neroli, both "bigarade" and from Portugal. The results varied extremely. Turkish oil of roses gave the greatest, the samples of oil of neroli the smallest, yield of crystalline diphenylurethane. Geraniol can be freed by Monnet's method from non-alcoholic constituents; it is heated with acetic anhydride at 140° for 8 hours, the acetates are purified and then hydrolysed with alcoholic potash, and the oil thus obtained is distilled under diminished pressure. Rhodinol is the chief constituent; a sample from Schimmel of Leipzig was found to owe its less pleasant odour to the presence of chlorine compounds, so that commercial geraniol stands in much the same relation to pure rhodinol as does synthetical benzaldehyde to oil of bitter almonds. Commercial rhodinol, from the Société Chimique des Usines du Rhône at Lyon yielded a rhodinol identical with that obtained from geraniol; the heat of combustion is 3026 Cal. in both cases. Mixed with the rhodinol is citronellol, $C_{10}H_{19}\cdot OH$, which was isolated and converted into derivatives. *Citronellylic hydrogen phthalate* resembles the rhodinylic compound but is more stable; the *silver* salt melts at 120—124°; the liquid *methylic* salt was also prepared, and so was liquid *citronellylic diphenylurethane.*

Preparation of Menthylic Carbonate.—Menthol (30 grams) is dissolved in chloroform (30 c.c.), pyridine (25 c.c.) is added, the whole cooled by a freezing mixture, and 55 grams of a chloroform solution of carbonic chloride (containing 10 grams) slowly added; after being left for a day in the cold, the product is distilled with steam, and the solidified residue washed with hot water and recrystallised from alcohol. Menthylic carbonate melts at 105°.

Remarks.—Of these the most important is to the effect that the name *geraniol* must be abandoned, the substance being identical with *rhodinol*.

C. F. B.

Oil of Cloves. By ERNST ERDMANN (*J. pr. Chem.*, 1897, **56**, 143—156).—When oil of cloves is treated with an aqueous potash solution, a residue containing oxygen is left undissolved; this the author calls "échappés." It has no constant boiling point, and its sp. gr. is lower than that of oil of cloves; when treated with alcoholic potash, there is a rise in temperature, and on extracting with ether caryophyllene is obtained. The residual alkaline liquid contains eugenol and acetic acid.

When "echappés" is distilled under a pressure of 12 mm. at a temperature of 142°, a solid substance collects in the receiver; this is found to be acetyleugenol, thus accounting for the fact that the portion of oil of cloves insoluble in dilute potash solution contains oxygen.

Acetyleugenol, prepared by treating pure eugenol with acetic anhydride, boils at 145—146° (8·5 mm.), has a sp. gr. = 1·0842 at 15°, is volatile with steam, and crystallises from alcohol in large, rhombic plates melting at 29°.

Thom's method (*Verhandl. der Gesellsch. Deutsch. Natur. f. w. Aerzte*, 1891, 184) for estimating the value of oil of cloves, and which presupposes the existence of free eugenol in the oil, gives numbers which are too low, because the acetyleugenol is only partially estimated when this method is employed; if, however, the oil of cloves be first saponified, the true value can be obtained.

When oil of cloves is treated with alcoholic potash, and the free alkali titrated with normal hydrochloric acid, using litmus as indicator, it is found that a greater amount of alkali has been used up than is accounted for by the presence of acetyleugenol; this is because salicylic acid is present in small amount, probably combined with eugenol as acetylsalicylic acid.

The author has further proved the presence of furfuraldehyde in oil of cloves.

A. W. C.

Ethereal Oil of Angostura-bark. By HEINRICH BECKURTS and JULIUS TROEGER (*Arch. Pharm.*, 1897, **235**, 518—535).—This ethereal oil is obtained from the dark-brown oily liquid left after the alkaloids have been removed from the ethereal extract of the bark by shaking it with dilute sulphuric acid. The residue left is distilled with steam and the portion of the distillate insoluble in water is dried by means of anhydrous sodium sulphate; it is a yellowish oil which becomes darker after a time, and has an aromatic taste and odour; it is easily soluble in the ordinary organic solvents. Its physical properties agree with those of Schimmel and Co.'s preparation, and according to this firm the bark yields 1·5 per cent. of pure oil. The crude oil has

a rotatory power in a Wild's polaristrobometer $= -50°$ (100 mm. tube); sp. gr. $= 0.941$ at $20°$; refractive index $n_D = 1.50624$. The analytical results obtained with different specimens were not concordant; this is also the case with oils from cubebs, preparations from old plants containing cubeb camphor, whilst those from younger plants consist essentially of terpene.

Attempts to isolate the substances contained in the oil, by fractional distillation both at the ordinary pressure and under diminished pressure, failed to give satisfactory results, owing to elimination of water arising from decomposition of the alcoholic constituent of the oil. In one distillation at the ordinary pressure, however, analysis of the fraction boiling at 260—270°, of which the major portion distilled at 264—265°, showed a composition corresponding with galipene alcohol, $C_{15}H_{26}O$, and on heating with acetic anhydride this fraction gave galipene, $C_{15}H_{24}$. *Galipene alcohol*, which is soluble in the ordinary solvents, does not possess the characteristic odour of the crude oil, and is optically inactive; sp. gr. $= 0.9270$ at $20°$; refractive index $n_D = 1.50624$. By the action of phosphorus pentachloride, a clear oil of pleasant odour and containing chlorine is obtained.

Galipene, obtained by the action of acetic anhydride on the alcohol or on the fractions boiling at 250—280°, is a yellowish oil which boils between 256° and 260°, the major portion distilling at 258—259°. It is more mobile than the crude oil, and has a fainter odour. It is soluble in the ordinary solvents; sp. gr. $= 0.9110$ at $20°$; rotatory power $= 18°$ (100 mm. tube); refractive index $n_D = 1.50374$. The *hydrochloride*, $C_{15}H_{24},2HCl$, is obtained by the action of hydrogen chloride dissolved in acetic acid; this solution does not at first mix with the terpene, but there is a dark-red zone of demarcation; the upper portion then gradually becomes violet and the lower red, and finally, after several days, mixture may be effected by shaking. The hydrochloride crystallises in transparent prisms and melts at 114—115°; the *hydrobromide* crystallises in lustrous, prismatic needles and melts at 123°.

The fraction of the crude oil boiling at 260—265° was in one instance green; analysis indicated the composition of a terpene, and the hydrobromide prepared from it melted at 124°.

When the residue left after distillation at 280° under the ordinary pressure, or at 200° under 92 mm. pressure, is shaken with alcohol, it leaves a dirty green to yellowish-white, amorphous substance which is insoluble in cold alcohol, easily soluble in ethylic acetate, ether, and light petroleum, and partly soluble in acetic acid. It does not show a constant melting point, decomposes at 110—120°, becoming brown or black, and then melts at 130—140°. From the analysis, it appears to be a substance containing oxygen and formed from the alcohol by distillation.

Since the crude oil is lævorotatory, the alcohol inactive, and the terpene dextrorotatory, it is probable that in the isolation of the terpene from the crude oil an inversion is effected, and that the terpene contained in the oil has a rotatory power different from that of the terpene obtained from it by means of acetic anhydride.

E. W. W.

Sinigrin, Sinalbin, Sinapin, Sinapic Acid. By JOHANNES GADAMER (*Ber.*, 1897, **30**, 2322—2327; 2327—2328; 2328—2330;

2330—2334).—The main facts in these papers have already appeared (Abstr., 1897, i, 254 and 360).

Glucosides contained in the Root of Helleborus niger: Helleborein and Helleborin. By K. THAETER (*Arch. Pharm.*, 1897, **235**, 414—424).—Of these glucosides, the former is easily soluble in water, but insoluble in ether, and the latter is insoluble in water but soluble in ether.

Helleborein is obtained from the aqueous extract by preparing from it the tannin compound of the glucoside and treating this with lead hydroxide, which liberates the glucoside; this is purified by repeated solution in absolute alcohol, and precipitation by ether. From a solution in 96 per cent. alcohol, only a yellow, amorphous, very hygroscopic mass separates, but from absolute alcohol fine needles are obtained which, although not as hygroscopic as Husemann and Marmé's preparation, have the same physical properties. The author's analysis, however, indicates an empirical formula, $C_{37}H_{56}O_{18}$, and the analysis of the blue product, which Husemann and Marmé named helleboretin, corresponds with the formula $C_{19}H_{30}O_5$; this can be obtained from helleborein by the action of dilute hydrochloric or sulphuric acid, dextrose and acetic acid being also formed. The acetic acid is not derived from a secondary action of the mineral acid on helleboretin, for the latter is not affected by dilute sulphuric acid. By fusion with alkalis, helleboretin yields formic acid and a substance which is soluble in alcohol and ether, but gives no colour reaction with ferric chloride. By oxidising helleboretin with chromic acid mixture, and subsequently distilling with steam, a distillate containing formic acid, and probably higher homologues of this acid, is obtained; a white substance insoluble in water and acids, but easily soluble in alcohol, is left in the retort; this gives no coloration with ferric chloride. With concentrated nitric acid, helleboretin gives an intensely violet solution which deposits violet flakes on pouring it into water and allowing it to stand. Neither dilute nor concentrated nitric acid gives any coloration with helleborein, and no helleboretin is formed.

Husemann and Marmé's method of preparing helleborin did not prove successful, but the author obtained it from the ethereal extract by treating it with light petroleum to remove the fatty compounds, and then with acetone, which dissolves tarry and colouring matters. The residual helleborin can be purified by crystallisation from a mixture of ether and alcohol, and is then pure white; in its physical properties it agrees with those of Husemann and Marmé's preparation, and gives the characteristic violet-red coloration with concentrated sulphuric acid, but the author's analysis indicates an empirical formula $C_6H_{10}O$. E. W. W.

Substances contained in the Root of Baptisia tinctoria R.Br. ψ-Baptisin. By K. GORTER (*Arch. Pharm.*, 1897, **235**, 494—503. Compare Abstr., 1897, i, 625).—*ψ-Baptisin*, $C_{27}H_{30}O_{14}$, is obtained from Merck's baptisin by crystallisation first from dilute alcohol, then from hot water, and finally from dilute spirit. It crystallises in colourless needles, is tasteless, and contains neither nitrogen nor

water. It melts at 247—248°, is soluble in boiling water, alcohol of 50 per cent. or acetone, very soluble in methylic alcohol, but insoluble in cold water, ether, acetone, benzene, chloroform, and dilute spirit, the specific rotatory power $[\alpha]_D = -101° 40'$. With sulphuric acid, it gives a yellowish-brown coloration passing into orange-red; with Erdmann's reagent a very fugitive green coloration passing through reddish-violet to reddish-brown, and becoming green on addition of water; with a solution of iodic acid in concentrated sulphuric acid, it gives successively violet, red, olive-green, and yellow colorations. Millon's reagent produces a pale red coloration on boiling, and ferric chloride colours a solution in methylic alcohol yellowish-brown. It does not reduce Fehling's solution even on boiling with it for a short time, but reduction takes place with ease after it has been treated with sulphuric acid. From dilute alcohol, it crystallises with $7\frac{1}{2}H_2O$ or $4H_2O$, and, after drying over sulphuric acid, it contains $1\frac{1}{2}H_2O$, which may be driven off at 125—130°, the substance becoming slightly yellow. A solution of ψ-baptisin in methylic alcohol after a time deposits crystals of an additive product, $C_{27}H_{30}O_{14}$,MeOH + $1\frac{1}{2}H_2O$, which is insoluble in water, methylic alcohol, chloroform, and ethylic acetate, and loses both methylic alcohol and water if kept over sulphuric acid.

By boiling ψ-baptisin with dilute sulphuric acid, *ψ-baptigenin*, $C_{15}H_{10}O_5$, glucose, and rhamnose are formed. The first is a white, crystalline compound, does not melt below 270°, is insoluble in cold water, acetone, methylic and ethylic alcohols, but soluble in hot acetone and hot methylic alcohol. By mixing with 5 per cent. sodium hydroxide solution, a fine, crystalline, sodium compound is obtained, which is soluble in water but can be salted out by sodium chloride. ψ-Baptigenin dissolves in ammonia on slightly warming, forming a solution which gives a precipitate with lead acetate, but does not reduce ammoniacal silver nitrate solution. Baptigenetin and formic acid are produced on boiling ψ-baptigenin with 5 per cent. sodium hydroxide solution.

Acetyl-ψ-baptigenin, $C_{15}H_9O_5Ac$, melts at 173°, is insoluble in cold water, alcohol of 95 per cent., and light petroleum, but easily soluble in ethylic acetate, benzene, and acetone. On boiling with sodium hydroxide solution, baptigenetin is formed, but under certain conditions not yet determined, not baptigenetin but a substance which is probably *methylbaptigenetin* is obtained; the latter melts at 129—130°, crystallises in thin needles, and in alcoholic solution gives a red coloration with ferric chloride solution. E. W. W.

Filicic Acids. By Rudolf Boehm (*Chem. Centr.*, 1896, ii, 1036—1038; from *Arch. exp. Path. Pharm.*, **38**, 35—58).—In extracts of *Filix mas.* (male fern), the ethereal oil and filicic acid are not the only active ingredients. After mixing the extract with magnesia, and extracting with water, sulphuric acid added to the extract causes a voluminous precipitate; if this is dissolved in alcohol, crystals of *aspidin*, $C_{23}H_{32}O_7$, separate after a time; it has reducing properties, and contains a methoxyl group. It is a poison acting chiefly on the central nervous system. From the alcoholic mother liquor, another

crystalline compound, *albaspidin*, $C_{22}H_{28}O_7$, crystallises out. It contains no methoxyl group, and its physiological action resembles that of filicic acid.

From the mother liquor after the separation of this substance, a monobasic acid *flavaspidic acid*, $C_{23}H_{28}O_8$, was separated; it crystallises in slender, golden-yellow prisms, and melts at 157—159°. Other substances obtained are *aspidinin*, crystallising in colourless, silky, rhombic tablets, and melting at 110°, and *aspidinol*, $C_{12}H_{16}O_4$, crystallising in thick, rhombic, bright yellow prisms, and melting at 143°; the reactions of these are described.

By heating filicin (filicic acid) for 8 hours with 15 per cent. sodium hydroxide, phenol, phloroglucinol, and a new acid, *filicinic acid*, $C_{11}H_{14}O_4$, were obtained. The latter crystallises in cubes or octahedrons, melts at 215°, and on oxidation yields dimethylmalonic acid. The *methylic* salt melts at 208°, and the *ethylic* salt at 215°. W. D. H.

Cantharidin. By HANS MEYER (*Monatsh.*, 1897, **18**, 393—410).—By neutralising a solution of cantharidin in water with caustic potash, using phenolphthalein as indicator, it is shown to contain one free carboxyl group. In order to determine the functions of the other two oxygen atoms, the cantharidin was treated with sodium methoxide and methylic iodide, when a dimethyl derivative was obtained; this was also produced on the etherification of cantharidin which had been exactly neutralised with caustic potash, but no monomethyl derivative was formed. The second methyl group must have replaced the hydrogen of a carboxyl or of a hydroxyl group. If the latter, then cantharidin should be capable of being acetylised, but this is not the case, and, moreover, if a hydroxyl group, then the fourth oxygen atom must belong to a ketone group, which is disproved by the facts given below. It appears probable, therefore, that the second methyl group is attached to carbonyl, which is explained by the presence of a lactone group, the latter being split at the moment of etherification. The hydroxyl group thus formed is attached to a tertiary carbon atom, since it does not react with acetic anhydride and sodium acetate, as it should do if it were a secondary one.

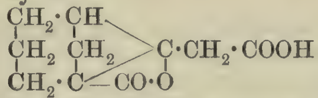
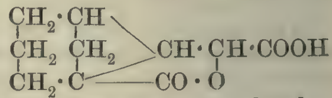
Homolka's observation (*Ber.*, 1885, **18**, 987), that cantharidin must contain a ketone group, because cantharic acid, when treated with zinc chloride and dimethylaniline, condenses with formation of a green colouring matter, is not justifiable, especially as a similar reaction has been observed with many anhydrides, lactones, and dicarboxylic acids. Moreover, if cantharidin contains a ketone group, so must its dimethyl derivative, but it was found to be impossible to prepare a hydrazone from the latter.

The substance formed by the action of hydroxylamine on cantharidin is an oximide, and by the action of phenylhydrazine an acid hydrazide is obtained and not a hydrazone as stated by Anderlini (Abstr., 1890, 640), and Spiegel (Abstr., 1892, 999; 1893, i, 40); this conclusion is supported by the fact that when cantharidin is heated with alcoholic ammonia, an imide $\left\{\begin{array}{l} CO- \\ C\cdot OH \\ CO- \end{array}\right\rangle NH$ is produced, in which

the hydrogen of the imide group can be replaced by methyl, yielding the same substance as is formed by the action of methylamine on cantharidin; and also when the phenylhydrazide of cantharidin is nitrated and the product reduced :—

$$\left\{\begin{matrix} CO- \\ C\cdot OH \\ CO- \end{matrix}\right\rangle N\cdot NH\cdot C_6H_4\cdot NO_2 + 8H = \left\{\begin{matrix} CO- \\ C\cdot OH \\ CO- \end{matrix}\right\rangle NH + C_6H_4(NH_2)_2 + 2H_2O.$$

From these considerations it appears probable that cantharidin is represented by the formulæ I, and the isomeric monobasic cantharic acid by II.

I.  II. 

Dimethylcantharidin separates from chloroform in large, colourless, glistening crystals melting at 81—82°, can be distilled without decomposition under atmospheric pressure, when it boils at 296—298° (uncorr.), and is readily soluble in ether, alcohol, benzene, chloroform, pyridine, and boiling water.

Cantharidic acid phenylhydrazide, prepared by heating cantharidin with phenylhydrazine in molecular proportion at 200—220°, separates from acetone in small, glistening crystals melting at 236—238°. It gives Bulow's reaction for acid hydrazides and reduces Fehling's solution with liberation of nitrogen. A. W. C.

A Nitrogen Compound from the Buds of Ricinus communis. By ERNST SCHULZE (*Ber.*, 1897, **30**, 2197—2198).—A well-defined crystalline compound containing nitrogen, *ricidine*, $C_{12}H_{13}N_3O_3$, can be extracted from the dried buds of *Ricinus communis*, by treatment with 95 per cent. alcohol. It is sparingly soluble in water, but dissolves on warming, and separates again on cooling in small, colourless prisms melting at 193°, and differs from convicine in being soluble in hot alcohol, and not being precipitated by mercuric nitrate. The compound is present in the buds in considerable quantity. J. F. T.

Dipyridine Methyleniodide. By S. H. BAER and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1896, **18**, 988—989).—The additive compound of pyridine and methylenic iodide is best prepared by the following method. The two are mixed in molecular proportion, an equal volume of alcohol is run in, and the whole heated for an hour on the water bath; after recrystallising the product from alcohol (50 per cent.), *dipyridine methyleniodide*, $(C_5NH_5)_2CH_2I_2$, is obtained in the form of slender, yellow needles decomposing at 220°. It is soluble in water, but insoluble in cold alcohol, ether, benzene, or chloroform.

Dipyridine ethylenbromide, $(C_5NH_5)_2C_2H_4Br_2$, crystallises in colourless plates melting and decomposing at 295°.

Monopyridine compounds with methylenic iodide and ethylenic bromide could not be obtained. J. J. S.

β-Toluoylpicolinic Acid and β-Tolyl Pyridyl Ketone. By ALEXANDER JUST (*Monatsh.*, 1897, **18**, 452—459).—*β-Paratoluoylpicolinic acid*, $C_{14}H_{11}NO_3$, produced by the action of aluminium chloride on a solution of quinolinic anhydride in toluene, crystallises from

alcohol in microscopic, rhombic prisms melting at 166°, with evolution of carbonic anhydride; the air-dried crystals are anhydrous, and easily soluble in hot water and alcohol, but insoluble in benzene, ether, and chloroform. The *hydrochloride* crystallises in tufts of needles, the normal *silver* salt in microscopic crystals, and the *acid silver* salt in large, colourless, rhombic crystals.

β-Paratolylpyridylorthoxazinone, $C_{14}H_{10}N_2O_2$, obtained by the interaction of the above acid with hydroxylamine hydrochloride, forms colourless crystals melting at 217° with partial sublimation; it is insoluble in sodium carbonate.

1-*Phenyl-3-paratolylquinolinazone*, $C_{20}H_{15}N_3O$, obtained by the action of phenylhydrazine on toluoylpicolinic acid, crystallises in beautiful, yellow prisms melting at 247°; it is soluble in benzene, sparingly so in water and ether, and insoluble in sodium carbonate solution. The *hydrochloride* and *platinochloride* are both yellow, crystalline substances.

β-Paratolyl pyridyl ketone is formed when toluoylpicolinic acid is heated at its melting point, carbonic anhydride being given off. It is very readily soluble in alcohol and benzene, but only sparingly in light petroleum and water; from dilute alcohol, it separates in colourless crystals melting at 78°.

The *hydrochloride* crystallises in needles, which are exceedingly soluble in water; the *platinochloride* in beautiful, yellow crystals; and the *oxime* in small, rhombic prisms melting at 167°. A. W. C.

Diacetyl-lutidine. By Max Scholtz (*Ber.*, 1897, **30**, 2295—2299).—Acetylacetone (50 grams) and 40 per cent. formaldehyde (20 grams) readily condense in the presence of a few drops of piperidine to form *methylenediacetylacetone*, $CHAc_2 \cdot CH_2 \cdot CHAc_2$; this is a clear, syrupy liquid, and when saturated with ammonia at 0°, yields *diacetyldihydrolutidine*, $CH_2 <^{CAc:CMe}_{CAc:CMe}> NH$, which crystallises from alcohol in yellow needles melting at 198°, and dissolves in concentrated sulphuric acid and in dilute hydrochloric acid on warming. When oxidised with nitrous acid, according to Hantzsch's method, it yields *diacetyl-lutidine nitrate*, $C_{11}H_{13}NO_2,HNO_3$, melting and decomposing at 117°, and readily soluble in water, more sparingly in alcohol. The *base*, obtained by the action of potassium hydroxide on the nitrate, crystallises from ether in large, colourless plates melting at 72°. The *platinochloride*, $(C_{11}H_{13}NO_2)_2,H_2PtCl_6 + H_2O$, melts at 179°, and the *aurochloride* at 167°; the *phenylhydrazone* is an oil, but the *di-phenylhydrazone hydrochloride*, $C_{11}H_{13}N(N \cdot NHPh)_2,HCl$, crystallises in needles. The *phenylhydrazone* of *diacetyl-lutidine nitrate* melts at 180°, and the corresponding *dihydrazone* at 232°. J. J. S.

β-Benzoylisonicotinic Acid. By Moriz Freund (*Monatsh.*, 1897, **18**, 447—451).—*β-Benzoylisonicotinic acid*, $C_{13}H_9NO_3$, obtained by the action of aluminium chloride on a mixture of benzene and cinchomeronic anhydride, crystallises from water or dilute alcohol in colourless needles melting at 210—211° and gradually turning yellow on exposure to air. The *copper* salt crystallises in pale blue needles.

The free acid, when heated at 240° under a pressure of 40 mm., sublimes without decomposition, and this makes it appear probable that the carboxyl group is in the γ-position, a supposition which is proved by the fact that, on heating the acid with excess of lime, pyridine is produced. In a second experiment, using 2 parts of lime to 1 of the acid, no pyridine was obtained, but only a heavy yellow oil which consisted of β-phenyl pyridyl ketone, thus definitely proving the constitution of the original acid. A. W. C.

Action of Hydrogen Peroxide on Tetrahydroquinoline and Tetrahydroisoquinoline. By EMIL MAASS and RICHARD WOLFFENSTEIN (*Ber.*, 1897, 30, 2189—2192).—In spite of many statements to the contrary, tetrahydroquinoline is not acted on by hydrogen peroxide, whilst tetrahydroisoquinoline alone yields *orthamidomethylphenylacetaldehyde*, $NH_2 \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot COH$; when pure, this forms white crystals melting at 76—77°; its *picrate* melts at 139°. The aldehyde, which readily polymerises on standing, yields tetrahydroisoquinoline on reduction with tin and hydrochloric acid. Sodium hydrogen sulphite readily reacts with it, forming *tetrahydroisoquinolinesulphonic acid*, which crystallises from alcohol and melts at 185—186°; the aldehyde yields a *benzoyl* compound which melts at 106—108° and reduces Fehling's solution. J. F. T.

Metamido-α-methylbenzimidazole, or Paramido-α-methylbenzimidazole. By ALFRED GALLINEK (*Ber.*, 1897, 30, 1909—1913. Compare Bamberger and Lorenzen, Abstr., 1892, 631).—It was anticipated that metamido-α-methylbenzimidazole,

$$NH_2 \cdot C_6H_3 <\begin{matrix} NH \\ N \end{matrix}> CMe,$$

and paramido-α-methylbenzimidazole, $NH_2 \cdot C_6H_3 <\begin{matrix} N \\ NH \end{matrix}> CMe$, would be formed by the reduction of orthonitracetylparaphenylenediamine and orthonitracetylmetaphenylenediamine respectively; these substances, however, yield the same anhydro-base, which is identical with Hobrecker's amidobenzimidazole (*Ber.*, 1872, 5, 923). This phenomenon appears to resemble the observations of von Pechmann (Abstr., 1895, i, 347).

The base crystallises from water in aggregates of small, transparent plates containing $2H_2O$, and melts indefinitely at 55—80°; the solution is alkaline, and has a bitter taste. The *hydrochloride* is very readily soluble in water, and crystallises in silky needles; the *nitrate*, which is also readily soluble, forms long needles, and melts at 195°; the *sulphate* crystallises in prisms, and melts at 274°, and the *picrate* at 207°. The *acetyl* derivative melts at 249° after crystallisation from water, but when alcohol is employed, the product melts at 324°. The silver derivative is white and amorphous.

Reduction of orthonitrodiacetylmetaphenylenediamine gives rise to the same base. When diazotised, and combined with phenols, the substance yields colouring matters capable of directly dyeing cotton (compare Abstr., 1894, i, 79, and 1896, i, 427). M. O. F.

Reduction and Oxidation Products of $\alpha\mu$-Dimethyloxazole and its Condensation with Acetaldehyde. By M. OESTERREICH

(*Ber.*, 1897, **30**, 2254—2260. Compare Schuftan Abstr., 1896, i, 262).—A better yield of *αμ*-dimethyloxazole is obtained when acetamide and chloracetone are heated together for 10 hours at 120—125°. When an alcoholic solution of the base is reduced with sodium (four times the theoretical quantity), the chief product is *αμ-dimethyloxalidine*, $C_5H_{11}NO$. The mixture is treated with water and any unaltered oxazole is removed when the alcohol is distilled off; the residue when distilled on a sand bath yields the oxalidine, which after being dried with potash boils at 159°. It is an extremely strong base, with an odour resembling that of piperidine, and is readily soluble in alcohol or ether. Its *platinochloride* crystallises in yellowish-red needles readily soluble in water and decomposes at 180°; the *picrate* crystallises in lemon-yellow needles melting and decomposing at 103—104°. *αμ-Dimethyloxazolidylphenylthiocarbamide*, $C_{12}H_{16}N_2OS$, crystallises from its alcoholic solution in rhombic plates melting at 145°. The corresponding *phenylcarbamide*, $C_{12}H_{16}N_2O_2$, crystallises in needles melting at 225°. *Benzoyl-αμ-dimethyloxazolidine*, obtained by heating oxazolidine with benzoic chloride for 3—4 hours at 140°, crystallises in colourless plates melting at 105°. *μ-Methyloxazole-α-carboxylic acid* is prepared by adding dimethyloxazole to boiling potassium permanganate solution (4 per cent.) until the permanganate is decolorised. It is most readily purified by conversion into its silver salt, which may then be decomposed by hydrogen sulphide. It crystallises from water in long, colourless needles melting at 287—288°, and readily soluble in water, alcohol, or ether.

Methylpyriculine, C_4H_5N, is formed when dimethyloxazole (30 grams) and acetaldehyde (18 grams), are heated in a Pfungst's autoclave at 140—145° for 10 hours; when the product is distilled with alkali, a liquid is obtained which, on saturation with potash, yields a small quantity of an oil boiling at 156—157°. It is sparingly soluble in water, readily in ether or alcohol, and has an odour resembling that of pyridine. The *platinochloride*, $(C_4H_5N)_2,H_2PtCl_6$, is a crystalline powder decomposing at 185°; the *aurochloride* crystallises in golden-yellow needles melting at 91—92°. The *picrate* melting and decomposing at 125°, the *phosphomolybdate*, *tannate*, and *mercuric chloride* derivatives are also described. J. J. S.

Nitro- and Amido-derivatives of Phenonaphthoxazone. By FRIEDRICH KEHRMANN and ERNST GAUHE (*Ber.*, 1897, **30**, 2130—2138). —The authors have prepared three isomeric amidophenonaphthoxazones in order to ascertain the influence of the position of the amido-group on the colour and tinctorial properties of the phenonaphthazones. The amido-compounds are prepared by the reduction of the nitro-derivatives, formed by the condensation of nitro-derivatives of orthamidophenol with hydroxynaphthaquinone. The yield of nitrophenonaphthazoxazone is always small, an anilide being invariably formed. 2-*Nitrophenonaphthoxazone*, $C_{10}H_5O{<}^{N}_{O}{>}C_6H_3{\cdot}NO_2$, prepared from 5-nitro-1:2-orthamidophenol, crystallises in yellowish-brown needles or plates melting at 246—247°. 2-*Amidophenonaphthoxazone* crystallises in violet-black needles, which have a

metallic lustre, melts at 255—256°, and forms yellow solutions in dilute mineral acids. The *anilide* from hydroxynaphthaquinone and 5-nitrorthamidophenol, $C_{10}H_5O_2{\cdot}NH{\cdot}C_6H_3(NO_2){\cdot}OH$, crystallises in long, lustrous, red needles, which decompose at about 240°; it is decomposed by boiling dilute aqueous alkalis, but not by the alkali carbonates. The *sodium* derivative crystallises in small, readily soluble, black needles. 3-*Nitrophenonaphthoxazone* crystallises in yellowish-brown needles which have a brassy lustre and melt at 253—254°; it yields fluorescent, yellow solutions in acetic acid and benzene, differing in this respect from its two isomerides. 3-*Amidophenonaphthoxazone* forms green needles, which have a strong metallic lustre, and decompose at 280° without melting; it yields fluorescent solutions when dissolved in the mineral acids or in a mixture of alcohol and benzene. The *anilide* crystallises in violet plates which decompose at about 270°.

A third nitro-compound of unknown constitution, obtained by the action of nitric acid on phenonaphthoxazone (Abstr., 1895, i, 245), melts at 234—235°, and not at 232° as previously stated, and is non-fluorescent; the corresponding *amido*-compound forms dark red, spherical aggregates of needles melting at 211—212°, the acid solutions of which are yellowish-green, and show no fluorescence. The nitro-amidophenol, which was thought by Friedländer and Zeitlin (Abstr., 1894, i, 184) to be most probably 6-nitrorthamidophenol, does not yield a phenonaphthoxazone with hydroxynaphthaquinone, but only forms an *anilide*, $C_{10}H_5O_2{\cdot}NH{\cdot}C_6H_2(NO_2){\cdot}OH$, which crystallises in light red plates.

Experiments which will be described in a separate communication have shown that the nitro-compound is in reality 6-nitroparamidophenol. A. H.

Oxydichloropurine. By EMIL FISCHER and LORENZ ACH (*Ber.*, 1897, **30**, 2208—2219).—When potassium urate is heated with phosphorus oxychloride at 160—170°, 8-*oxy*-2 : 6-*dichloropurine*, $\begin{array}{l}N{:}CCl{\cdot}C{\cdot}NH\\ \;| \qquad\;\; \| \\ CCl{:}N{\cdot}C{\cdot}NH\end{array}\!\!>\!CO$, is formed, which closely resembles methyloxydichloropurine (Abstr., 1884, 996, 1308); it is best obtained pure by decomposition of the *ammonium* salt, which crystallises in faintly yellow plates. It decomposes above 350° without melting, and dissolves in about 120 parts of boiling alcohol or 1000 parts of boiling water. It is readily soluble in alkalis, and dissolves in concentrated sulphuric acid forming a solution from which it is precipitated by water, but when heated with concentrated hydrochloric acid at 120°, it is reconverted into uric acid. Methylic iodide converts the lead and potassium salts into 7 : 9-dimethyl-8-oxy-2 : 6-dichloropurine, and this reaction, therefore, furnishes a proof of the constitution of the compound. 7-Methyloxydichloropurine can be obtained by treating an alkaline solution of the potassium salt, at a low temperature, with methylic iodide in molecular proportion. 8-Oxydichloropurine is converted, by reduction with hydriodic acid and phosphonium iodide at 100°, into 8-*oxypurine*, $\begin{array}{l}N{:}CH{\cdot}C{\cdot}NH\\ \;| \qquad\;\; \| \\ CH{:}N{\cdot}C{\cdot}NH\end{array}\!\!>\!CO$, which is isomeric with hypoxanthine. It crystal-

lises in very slender, pliable needles, melts indefinitely at about 317° (corr.), and can be partially distilled at a higher temperature. It dissolves in alkalis and decomposes calcium carbonate, and also unites with mineral acids to form crystalline salts. The *hydriodide*, *hydrochloride*, and *hydrobromide* are all readily soluble, whilst the *nitrate* is only sparingly soluble; the *platinochloride* forms compact, yellow crystals, and the *aurochloride* slender, yellow plates. 8-Oxydichloropurine is converted by alcoholic ammonia at 150° into 6-*amido*-8-*oxy*-2-*chloropurine*, $\begin{array}{l}\mathrm{N:C(NH_2)\cdot C\cdot NH}\\ \mathrm{CCl:N\text{——}C\cdot NH}\end{array}\!>\!\mathrm{CO}$, which can be purified by conversion into the barium salt, from which it is obtained in very slender, matted needles. It carbonises above 360° without melting, and is soluble both in acids and alkalis. The *barium* salt crystallises in long, colourless, slender needles. The *sulphate* forms fascicular groups of needles, and the *hydrochloride* also crystallises in needles. The base, by reduction with hydriodic acid, is converted into 6-*amido*-8-*oxypurine*, $\begin{array}{l}\mathrm{N:C(NH_2)\cdot C\cdot NH}\\ \mathrm{CH:N\text{——}C\cdot NH}\end{array}\!>\!\mathrm{CO}$, which crystallises in microscopic needles and decomposes without melting when heated. The *sulphate* crystallises in oblique, four-sided plates and is sparingly soluble in water, whilst the *nitrate* is more readily soluble, and crystallises in slender needles. The base itself readily reduces ammoniacal silver oxide. When 8-oxydichloropurine is heated with aqueous ammonia, both the chlorine atoms are replaced by NH_2, and 2:6-*diamido*-8-*oxypurine*, $\begin{array}{l}\mathrm{N:C(NH_2)\cdot C\cdot NH}\\ \mathrm{C(NH_2):N\cdot C\cdot NH}\end{array}\!>\!\mathrm{CO}$, is formed; it crystallises with $1H_2O$ in colourless needles and decomposes above 380°. The *hydrochloride* crystallises in long, colourless needles, and is readily soluble, whilst both the *nitrate* and the *sulphate* are only sparingly soluble; the *platinochloride* forms yellowish-red plates.

6-Amido-8-oxypurine is converted by nitrous acid into 6:8-*dioxypurine*, $\begin{array}{l}\mathrm{NH\cdot CO\cdot C\cdot NH}\\ \mathrm{CH:N\cdot C\cdot NH}\end{array}\!>\!\mathrm{CO}$, which is isomeric with xanthine. It crystallises with $1H_2O$ in long, narrow, lustrous plates which decompose above 400°. It readily dissolves in alkalis, and forms a *barium* salt which crystallises in slender, sparingly soluble needles. It is easily oxidised by concentrated nitric acid, and does not yield alloxan when treated with potassium chlorate and hydrochloric acid. Methylic iodide converts it into 1:7:9-trimethyl-6:8-dioxypurine (Abstr., 1897, i, 642). A. H.

Trichloropurine. By EMIL FISCHER (*Ber.*, 1897, **30**, 2220—2225).—*Trichloropurine*, $\begin{array}{l}\mathrm{N:CCl\cdot C\cdot NH}\\ \mathrm{CCl:N\cdot C\text{—}N}\end{array}\!\geqslant\!\mathrm{CCl}$, which is formed when 8-oxydichloropurine is heated at 150—155° with 70 parts of phosphorus oxychloride, crystallises with $5H_2O$ in large plates, which become anhydrous at 110°. The dry substance at 187—189° (corr.) suddenly melts, and decomposes with evolution of gas. It dissolves in 70 parts of hot water, forming a strongly acid solution, and is not precipitated from solutions of its salts by acetic acid. The salts of the alkalis and alkaline earth metals are readily soluble, whilst the *zinc* salt is

insoluble. When it is heated with hydrochloric acid, trichloropurine is reconverted into 8-oxy-2 : 6-dichloropurine.

Methylic iodide converts it into a mixture of the two well-known methyltrichloropurines,

$$C_4N_2Cl_2{<}{}^{NMe}_{—N}{>}CCl, \text{ and } C_4N_2Cl_2{<}{}^{—N}_{NMe}{>}CCl.$$

Since it yields these two isomeric methyl derivatives, the original trichloropurine is probably tautomeric, in this respect resembling certain of the amidines (von Pechmann, Abstr., 1897, i, 515), with which it is, moreover, analogous in constitution. Under these circumstances it has been impossible to assign to it with certainty either of the two possible formulæ,

$$C_4N_2Cl_2{<}{}^{NH}_{—N}{>}C{\cdot}Cl \text{ and } C_4N_2Cl_2{<}{}^{—N}_{NH}{>}CCl.$$

It differs from its methyl derivatives in being strongly acid and in yielding up its chlorine atoms to bases in a different order. This circumstance has rendered it possible to synthesise xanthine, hypoxanthine, adenine, and guanine (compare following abstract).

A. H.

Synthesis of Xanthine, Hypoxanthine, Adenine, and Guanine. By EMIL FISCHER (*Ber.*, 1897, 30, 2226—2254. Compare the foregoing abstract, and Abstr., 1897, i, 267).—*Synthesis of Hypoxanthine.*—When trichloropurine is heated with normal aqueous potash, the chlorine atom in position 6 is removed, and 6-*oxy*-2 : 8-*dichloropurine* (dichlorhypoxanthine), $\begin{matrix}NH{\cdot}CO{\cdot}C{\cdot}NH \\ | \qquad\quad \| \\ CCl{:}N{-}C{—}N\end{matrix}{>}CCl$, is produced; this crystallises in colourless needles, becoming brown at above 350°, forms an acid solution in water, and yields crystalline salts with bases. Nitric acid slowly oxidises it, forming a solution which gives the murexide reaction. When reduced by means of hydriodic acid, it is converted into hypoxanthine; this dissolves in 69·5 parts of boiling water and in about 1400 parts at 19°. Since these numbers differ somewhat from those given by Strecker, and the other properties of the substance are not sufficiently characteristic for its certain identification, the dichlorohypoxanthine was converted by the action of methylic iodide into *dimethyldichlorohypoxanthine*, $C_7Cl_2H_6N_4O$; this crystallises in colourless needles and melts indefinitely between 252° and 263° (corr.). On reduction with hydriodic acid, it is converted into dimethylhypoxanthine, and the compound obtained in this way is identical in every respect with that prepared from adenine and from meat extract; it melts at 251—253° (corr.), and forms a characteristic compound with sodium iodide. The synthetical hypoxanthine is, therefore, identical with the natural product, and with that prepared from adenine.

Synthesis of Xanthine.—When trichloropurine is treated with alcoholic sodium ethoxide at the ordinary temperature, 6-*ethoxy*-2 : 8-*dichloropurine*, $\begin{matrix}N{:}C(OEt){\cdot}C{\cdot}NH \\ | \qquad\qquad \| \\ CCl{:}N{—}C{—}N\end{matrix}{>}CCl$, is formed; this crystallises in colourless, matted needles, and melts and decomposes at 203—204° (corr.). Hydriodic acid converts it into hypoxanthine. When the

trichloropurine is boiled with alcoholic sodium ethoxide, on the other hand, 2 : 6-*diethoxy*-8-*chloropurine*, $\begin{array}{l} \text{N:C(OEt)}\cdot\text{C}\cdot\text{NH} \\ \text{C(OEt):N}\cdot\text{C---N} \end{array}\!\!>\!\text{CCl}$, is formed. This crystallises in colourless, slender, matted needles, and melts and decomposes at about 209° (corr.); when reduced with hydriodic acid, it yields xanthine, identical in all respects with the natural product. Diethoxychloropurine, when heated with hydrochloric acid, yields *chloroxanthine*, $\begin{array}{l} \text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NH} \\ \text{CO}\cdot\text{NH}\cdot\text{C---N} \end{array}\!\!>\!\text{CCl}$, which is a colourless, granular, crystalline powder and carbonises when heated; its alkali salts are crystalline and soluble in water. Hydriodic acid converts it into xanthine. Methylic iodide converts chloroxanthine into chlorocaffeine, and from this caffeine and various other derivatives can be obtained, all identical with those from natural caffeine.

Synthesis of Adenine.—6-*Amido*-2 : 8-*dichloropurine* (dichloradenine), $\begin{array}{l} \text{N:C(NH}_2)\cdot\text{C}\cdot\text{NH} \\ \text{CCl:N----C---N} \end{array}\!\!>\!\text{CCl}$, obtained by the action of aqueous ammonia on trichloropurine, crystallises in stellate groups of microscopic needles, which become brown at above 300°. The alkali salts are crystalline and readily soluble in water. Hydriodic acid reduces it to adenine (6-amidopurine), $\begin{array}{l} \text{N:C(NH}_2)\cdot\text{C}\cdot\text{NH} \\ \text{CH:N----C---N} \end{array}\!\!>\!\text{CH}$, which is identical with the natural base; when rapidly heated in a narrow tube, it suddenly melts and decomposes at 360—365°.

When amidodichloropurine is heated with hydrochloric acid at 100°, it loses one atom of chlorine and forms 6-*amido*-2-*oxy*-8-*chloropurine*, which has not itself been isolated, but is converted by hydriodic acid into the 6-amido-2-oxypurine described below. When, however, the reaction is carried out at 120—125°, 6-*amido*-2 : 8-*dioxypurine*, $\begin{array}{l} \text{N:C(NH}_2)\cdot\text{C}\cdot\text{NH} \\ \text{CO}\cdot\text{NH---C}\cdot\text{NH} \end{array}\!\!>\!\text{CO}$, is formed as a colourless, crystalline powder, which carbonises above 360° without melting, and is very sparingly soluble in hot water. The crystalline *barium* salt is almost insoluble in water; the *hydrochloride* crystallises in compact prisms, and is decomposed by pure water; the *sulphate* is very sparingly soluble. It differs from the isomeric 2-amido-6 : 8-dioxypurine in being much more readily soluble in warm ammonia, and in yielding no guanidine when it is oxidised with sodium chlorate and hydrochloric acid.

6-*Amido*-2-*ethoxy*-8-*chloropurine*, $\begin{array}{l} \text{N:C(NH}_2)\cdot\text{C}\cdot\text{NH} \\ \text{C(OEt):N}\cdot\text{C---N} \end{array}\!\!>\!\text{CCl}$, which is formed by the action of alcoholic sodium ethoxide on amidodichloropurine, crystallises in colourless needles, and does not melt, but softens between 275—280° (corr.). Hydriodic acid converts it into 6-*amido*-2-*oxypurine*, $\begin{array}{l} \text{N:C(NH}_2)\cdot\text{C}\cdot\text{NH} \\ \text{CO}\cdot\text{NH---C---N} \end{array}\!\!>\!\text{CH}$, which is a white, amorphous mass, and carbonises when heated; it is only very slightly soluble in hot water, and almost insoluble in alcohol; its *sulphate* crystallises with $1H_2O$, and, like the other salts, is only sparingly soluble. 6-Amido-2-oxypurine closely resembles guanine, but does not yield

guanidine on oxidation, and can also be distinguished by the fact that guanine sulphate contains $2H_2O$. The constitution of adenine follows from that of 6-amidodioxypurine, but, as in the case of xanthine, it has so far been impossible to distinguish between the two possible tautomeric formulæ. Dichloradenine is converted by methylic iodide into a *methyldichloradenine*, which melts and decomposes at 253° (corr.); this is more readily soluble both in water and acids than dichloradenine, and forms crystalline salts. Hydriodic acid reduces it to 9-methyladenine, identical with that prepared by Krüger (*Zeit. physiol. Chem.*, 18, 434) by the direct methylation of adenine.

Synthesis of Guanine.—When 6-oxy-2 : 8-dichloropurine is heated with alcoholic ammonia, it yields chloroguanine, which, by the action of hydriodic acid, is reduced to guanine; the latter is in every respect identical with the natural product. A. H.

Crystallised Xanthine and Guanine. By IAN HORBACZEWSKI (*Zeit. physiol. Chem.*, 1897, **23**, 226—230).—Amorphous xanthine is dissolved in a little potash, the solution filtered, and diluted with distilled water at 60° so that 1 gram of xanthine is contained in 2 litres of the solution. The solution is then acidified with acetic acid, filtered rapidly, and allowed to cool slowly; after several days, the xanthine is deposited on the sides of the vessel in the form of colourless, glistening nodules which contain $1H_2O$. The crystals may also be obtained by using a somewhat stronger solution containing alcohol. They do not give up their water until heated to 125—130°.

A warm, dilute alkaline solution of guanine (1 : 2000) is mixed with about one-third of its volume of alcohol, acidified with acetic acid, and allowed to cool. The crystals of guanine which separate are anhydrous, and in appearance resemble creatinine-zinc chloride.

J. J. S.

Derivatives of Theobromine. By WILLEM VAN DER SLOOTEN (*Arch. Pharm.*, 1897, **235**, 469—490).—See Abstr., 1897, i, 382.

Oxidation of Ethyltheobromine by Potassium Chlorate and Hydrochloric Acid. By HERBERT POMMEREHNE (*Arch. Pharm.*, 1897, **235**, 490—494).—Ethyltheobromine, on oxidation with hydrochloric acid and potassium chlorate, yields methylamine, methylethylalloxan and *apoethyltheobromine*. The last forms tabular crystals and melts at 137—138°. E. W. W.

The Methiodides of Nicotine. By AMÉ PICTET and P. GENEQUAND (*Ber.*, 1897, **30**, 2117—2125).—Nicotine dimethiodide, which was shortly described by Stahlschmidt (*Annalen*, 1854, **90**, 222), crystallises in compact, light yellow prisms melting at 216°.

Nicotine methiodide, $C_{10}H_{14}N_2$,MeI, is obtained by mixing nicotine with methylic iodide, in molecular proportion, in methyl alcoholic solution; it is a light yellow, syrupy mass which cannot be made to crystallise. It is not decomposed by alkali carbonates, but when treated with silver oxide yields an alkaline solution, which probably contains the methohydroxide, and when evaporated with hydrochloric acid

leaves a residue of the *hydrochloride of nicotine methochloride*,

$$C_{10}H_{14}N_2,MeCl,HCl,$$

which is a colourless, deliquescent mass. The corresponding *platinochloride*, $C_{10}H_{14}N_2,MeHPtCl_6$, melts and decomposes at 266°. *Nicotine dihydriodide*, $C_{10}H_{14}N_2,2HI$, formed by the direct action of hydriodic acid on the base, crystallises in long, colourless needles melting at 195°. When boiled with nicotine in alcoholic solution, it is converted into the *hydriodide*, which, like the corresponding methiodide, is a pale yellow, uncrystallisable mass. The monhydriodide is converted by methylic iodide into the *hydriodide of nicotine isomethiodide*, $C_{10}H_{14}N_2,HI,MeI$, which crystallises in colourless plates melting at 209°; this compound is decomposed by sodium carbonate with formation of *nicotine iso-methiodide*, $C_{10}H_{14}N_2,MeI$, which crystallises in colourless plates melting at 164°. *Nicotine isomethochloride*, $C_{10}H_{14}N_2,MeCl$, forms a hygroscopic, radiating crystalline mass, and its *platinochloride* decomposes at 235—240° without melting. Silver oxide converts the isomethiodide into the corresponding *hydroxide*, which could not, however, be isolated.

The formation of two isomeric quaternary iodides from nicotine proves that the two nitrogen atoms of this alkaloid are both tertiary. When the isohydroxide, corresponding with the isomethiodide, is oxidised by potassium permanganate, it is converted into trigonelline,

O———CO
NMe:CH·C
CH:CH·CH (the methylbetaine of nicotinic acid), and this reaction shows that the two methiodides have the following formulæ,

$$\underset{\text{Methiodide.}}{C_5NH_4{\cdot}C_4H_7NMe_2I} \quad \text{and} \quad \underset{\text{Isomethiodide}}{C_5NH_4MeI{\cdot}C_4H_7NMe},$$

the nitrogen atom of the pyrrolidine ring being more basic than that of the pyridine ring. A. H.

Alleged Conversion of Cinchonine into Cinchonidine. By BENJAMIN H. PAUL and ALFRED J. COWNLEY (*Pharm. J. Trans.*, 1897, **58**, 141).—The authors have subjected pure cinchonine to the action of a solution of potash in amylic alcohol, in the manner described by Koenigs and Husmann (Abstr., 1896, i, 707), who claim to have converted 5 per cent. of the cinchonine into cinchonidine. They were not able to detect the slightest trace of cinchonidine in the product, and suggest that Koenigs and Husmann, in their experiments, employed cinchonine containing cinchonidine. E. C. R.

Conversion of Cinchonine into Isomerides by Means of Acids. By ZDENKO H. SKRAUP (*Monatsh.*, 1897, **18**, 411—417).—By the action of hydrochloric acid, cinchonine is partially converted into its isomerdes, isocinchonine, and pseudocinchonine, and partially into the additive product.

No similar action is noticed in the case of cinchotine, but when the so-called neutral cinchotine hydrochloride is acted on by sulphuric acid, a portion of the base is converted into a *sulphonic acid*, which is easily separated from the unchanged substance by taking advantage of its solu-

bility in 50 per cent. alcohol containing excess of ammonia. The sulphonic acid crystallises in clusters of needles or leaflets containing varying amounts of water of crystallisation; it is only sparingly soluble in either water or alcohol, but is soluble in a mixture of the two liquids. It is coloured yellow at 220° and melts at 245—246° with decomposition and disengagement of gas. The base liberated by ammonia from this sulphonic acid agrees in melting point, appearance, and other properties with pure cinchotine.

Cinchonine contains a double linking, which is not present in cinchotine, and the author suggests that the resolution of the former into its isomerides may in some way be connected with this fact, for which assumption he hopes shortly to produce further evidence.

A. W. C.

Double Chlorides of Cinchonamine. By Léon Boutroux and P. Genvresse (*Compt. rend.*, 1897, **125**, 467—469).—Cinchonamine hydrochloride in aqueous solution readily combines with the chlorides of cadmium, zinc, or copper, forming double salts which contain 2 mols. of the organic base and 1 mol. of the metal. The cadmium compound crystallises readily in thin, elongated, rectangular plates, with truncated extremities very similar in appearance to the crystals of cinchonamine nitrate; when slowly formed, the crystals are thicker and shorter rhombic prisms with the face g^1 predominant. The zinc salt crystallises in silky, rhombic prisms, in which also the face g^1 is predominant, whilst the cupric salt forms brick-red crystals. All the crystals are anhydrous; the zinc and cadmium compounds are somewhat soluble in boiling water, but are quite insoluble in presence of hydrochloric acid; the cupric salt is dissociated by water, especially on heating.

Ferrous, magnesium, barium, and calcium chlorides seem to form no analogous compounds.

C. H. B.

Retamine. By J. Battandier and Th. Malosse (*Compt. rend.*, 1897, **125**, 450—451).—The molecular weight of retamine as determined from the boiling point of its solution in ethylic alcohol is 268·8; the analytical results agree very closely with the formula $C_{15}H_{26}N_2O$. It forms two hydrobromides, $C_{15}H_{26}N_2O,HBr$ and $C_{15}H_{26}N_2O,2HBr$, and a hydriodide, $C_{15}H_{26}N_2O,2HI$, which crystallises readily. The sulphate crystallises from water with $4H_2O$, and from concentrated alcohol with $2H_2O$. Retamine salts of the type $R{\cdot}HBr$ are neutral to phenolphthalein, but salts of the type $R{\cdot}H_2SO_4$ are acid to this indicator. When the diacid salts are mixed with one equivalent of an alkali hydroxide, half the acid is removed, and the salts neutral to phenolphthalein are formed. Determinations of the molecular weight, by adding a known excess of acid to the retamine and then titrating back with an alkali hydroxide and phenolphthalein, give the number 250, which agrees with the formula $C_{15}H_{26}N_2O$.

C. H. B.

The Digitalis Alkaloids. By Heinrich Kiliani (*Arch. Pharm.*, 1897, **235**, 425—429).—In reply to Keller, the author states that digitalis leaves contain, in addition to digitoxin, another crystalline poison which is also soluble in chloroform, and gives a similar reaction with glacial acetic acid and sulphuric acid containing iron. This sub-

stance, which he names *digitophyllin*, $C_{32}H_{52}O_{10}$, is a glucoside, and crystallises from methylic alcohol in prisms or plates; it sinters at 224°, and melts and decomposes at 230—232°. It is not so easily attacked by dilute hydrochloric acid as digitoxin and is more insoluble, one part requiring more than 30 parts of methylic alcohol for solution. According to the author, digitophyllin is probably identical with the French "digitaline crystallisée." E. W. W.

Estimation of Alkyl Groups Attached to Nitrogen. By JOSEF HERZIG and HANS MEYER (*Monatsh.*, 1897, **18**, 379—392. Compare Abstr., 1896, i, 68).—The authors now show that their method may be used for estimating alkyl groups attached to nitrogen, not only in the hydriodides, but in all salts and double salts of bases that are not explosive and that do not contain sulphur. A number of substances have been examined with results which do not in all cases agree with the observations of other investigators.

Pilocarpine cannot be considered as a dihydroxy-derivative of cytisine, because the latter contains no alkyl group attached to nitrogen, whereas pilocarpine contains an alkyl group (compare van der Moer, Abstr., 1890, i, 657). Pilocarpidine contains no alkyl group attached to nitrogen.

Morphine, apomorphine, scopolamine, and chelidonine each contain one methyl group.

Both the crystalline and amorphous varieties of bebirine contain one methyl and one methoxy-group, but no methyl connected to nitrogen.

Corydaline and bulbocarpine contain respectively four and one methyl groups (compare Dobie and Lander, Trans., 1892, 244 and 605, and Freund and Josephi, Abstr., 1894, i, 100).

Morphothebaine methiodide contains one methoxy- and two methyl groups, whilst stachhydrine and eserine each contain two methyl groups.

The authors point out that their method does apparently in some cases indicate more alkyl groups than are actually present, but such instances are of rare occurrence. A. W. C.

Intervention of Manganese in Oxidations produced by Laccase. By GABRIEL BERTRAND (*Compt. rend.*, 1897, **124**, 1032—1035).—The ash of laccase, as the author has previously stated, contains a relatively large proportion of manganese; in one case, it amounted to as much as 2·5 per cent. of the ash. Fractional precipitation of the laccase gave products with different activities, and it was found that the activity increased with the quantities of manganese present. Attempts to obtain laccase free from manganese were unsuccessful, but a laccase extracted from lucerne contained very little of this element, and had very little oxidising power; on adding a small quantity of manganese sulphate, however, its oxidising power, as measured by means of quinol solution, became more than thirty times as great. Iron, aluminium, cerium, zinc, copper, calcium, magnesium, and potassium have no effect similar to that exerted by manganese. It seems probable that manganese, which exists in small quantities in living organisms, has important functions that have hitherto been unrecognised, probably because the proportion of the element usually present is so minute. C. H. B.

Chemical Behaviour of Diastase and Occurrence of an Araban in Ordinary Diastase. By Augustin Wróblewski (*Ber.*, 1897, **30**, 2289—2295).—Finely ground malt is extracted first with 68 per cent. alcohol and then twice with 45 per cent. alcohol. On the addition of alcohol to the latter extract, the diastase is precipitated, the operation of solution in 45 per cent. alcohol and precipitation is repeated, and then the diastase is dissolved in water and salted out with magnesium sulphate; it is freed from sulphate by dialysis and then precipitated by alcohol and ether. The diastase thus obtained is soluble in water, gives no colour with iodine, and has a strong diastatic action. It gives all the reactions for albumin with the exception of the biuret reaction, and does not reduce Fehling's solution. Aqueous solutions yield a voluminous precipitate with potassium mercury iodide aud dilute hydrochloric acid; the filtrate from this, on the addition of alcohol, gives a precipitate consisting of araban. This carbohydrate has no diastatic action, is strongly lævorotatory, and on hydrolysis yields arabinose which is dextrorotatory; ordinary diastase consists mainly of this carbohydrate. The other constituent is a proteid which is precipitated by Brücke's reagent; it gives the ordinary proteid reactions, but yields no precipitate with lead acetate. When freshly prepared, it dissolves in water, but after treatment with alcohol it becomes insoluble, whilst a mixture of the soluble and insoluble varieties is obtained by boiling the commercial diastase with dilute sulphuric acid. Both varieties, when hydrolysed with 20 per cent. hydrochloric acid yield ammonia, nitrogen bases, leucine, and tyrosine, but no arginine. The author comes to the conclusion that diastase is a proteid substance, and he thinks that enzymes form a sub-class of the proteids.

J. J. S.

Action of Halogens on Albumin. By F. Gowland Hopkins (*Ber.*, 1897, **30**, 1860—1862).—Chlorine and bromine react in the cold with a solution of egg-albumin which has been freed from globulin, yielding voluminious precipitates, and a similar reaction takes place with iodine at 40—50°; after well washing and dialysing, the products obtained leave no ash on incineration, but contain halogen. The chlorine and bromine derivatives dissolve readily in a 5 per cent. solution of sodium carbonate, the iodine derivative somewhat more slowly; and from these solutions, acetic acid precipitates derivatives which still contain halogen, and which yield constant results on analysis. After 48 hours' dialysis, the chlorine compound prepared in this way contained 3·50—3·67 per cent. of chlorine, the bromine derivative 3·84 per cent. of bromine, and the iodine compound 6·11 to 6·29 per cent. of iodine. These compounds are insoluble in alcohol, ether, or benzene, and give the xanthoprotein and biuret reactions, but produce no coloration with Millon's reagent, neither do they blacken lead acetate solution when boiled with it. From the original precipitates produced by the action of the halogens on albumin, alcohol is capable of extracting substances rich in halogen, which appear to have a definite composition; these are precipitated from alcoholic solution on the addition of ether, and are sparingly soluble in water. Like the first-mentioned compounds, they give the xantho-

protein and biuret reactions, but no coloration with Millon's reagent. All the substances prepared differ from Paal's halogen peptones (Abstr., 1892, 895; 1894, i, 559) in their insolubility in water, in their acidic properties, and in showing no tendency to dialyse when in solution. F. G. H.

Preparation of Deuteroalbumose. By SIGMUND FRÄNKEL (*Monatsh.*, 1897, **18**, 433—436).—Deuteroalbumose free from protalbumose may be obtained from different peptone preparations by the following method.

Copper sulphate is added to the peptone solution, when a sticky precipitate of protalbumose separates; the supernatant liquid is cloudy but becomes clear on standing. The clear solution is freed from copper by precipitation with barium ferrocyanide, evaporated, and poured into absolute alcohol; after being collected on a filter, the residue is washed with alcohol and ether, and dried. A. W. C.

Animal Gum. By OTTO FOLIN (*Zeit. physiol. Chem.*, 1897, **23**, 347—362).—Animal gum is the name given by Landwehr to the carbohydrate material of the formula $C_{12}H_{20}O_{10}$, which he obtained from mucin and mucinoid substances. In the case of cartilage, however, Schmiedeberg has shown that the so-called animal gum contains both nitrogen and sulphur, and is, in fact, a mixture of chondroitin and chondroitin-sulphuric acid. Other observers have also noted the presence of nitrogen in this supposed carbohydrate.

In the present research, Landwehr's mode of procedure was followed as closely as possible; the submaxillary gland was used. Various details of difference in the results obtained are noted, and the end-product obtained contained 10—12 per cent. of nitrogen. The process was then repeated, using pure mucin prepared from the submaxillary gland; the end-product here also contained over 11 per cent. of nitrogen. The procedure of heating at 110—150°, which is adopted, converts mucin into a mucin-albumose, and this is precipitable by ferric chloride like the so-called animal gum. It is, however, possible, by the use of acids, to obtain from mucin a reducing substance free from nitrogen, and yielding a crystalline osazone; further details of this part of the work are promised. W. D. H.

Behaviour of Proteids with Aldehydes. By ERNST O. BECKMANN (*Chem. Centr.*, 1896, ii, 930—932; from *Forsch.-Ber. üb. Lebensm.*, &c., **3**, 324. See Abstr., 1895, ii, 375).—With H. SCHARFENBERGER GEN. SERTZ.—To convert 1 gram of gelatin into the insoluble modification, the aqueous solution is mixed with 5—6 drops of 40 per cent. formalin and evaporated on the water bath; 1—2 drops more of formalin are added and the residue is heated for 1—1½ hours at 100°, then digested twice or thrice with water at 60—70°, and dried at 100° until constant. Free acids should previously be neutralised by shaking with precipitated calcium carbonate. A solution of gelatin, which has been deprived of its power of gelatinising by heating for 30—35 hours, nevertheless yields its gelatinose in the insoluble form when treated with formalin. Similarly, albumin, hemialbumose, casein, and protein are rendered insoluble, diastase only to a small extent, whilst gelatin-peptone, albumin-

peptone, and tryptone remain soluble. The method, therefore, serves to show how far the peptonising process has progressed in commercial meat peptones, also to detect gelatin or albumin in meat extracts and sausage meat. Milk to which gelatin-fat emulsion has been added yields little more insoluble residue than pure milk (under $\frac{1}{2}$ per cent.). Formalin-gelatin is, however, completely dissolved by 12 hours' contact with sulphuric acid (1·34 sp. gr.); formalin-casein remains undissolved. Milk should be coagulated by adding a few drops of lactic acid, precipitated by alcohol, the lactose removed by alcohol, the alcohol expelled, the residue extracted with water, the solution neutralised with calcium carbonate and treated with formalin.

With O. Elsner.—Acraldehyde behaves like formalin; acetaldehyde does not, except in the absence of water. Acetaldehyde vapour, or its solution in alcohol, benzene, or acetone, slowly hardens dry gelatin films; the acetals have a similar action. Schleich's formalin-gelatin and Blum's protogen (formalin-albumin) have already been introduced into pharmacy. M. J. S.

Products of the Trypsin-fermentation of Casein. By Franz Röhmann (*Ber.*, 1897, 30, 1978—1981).—Calf's pancreas (1500 grams) was extracted with chloroform water at 35°, the extract made up to 5 litres; 25 grams of sodium carbonate and 50 c.c. of a 10 per cent. alcoholic solution of thymol were next added, and finally, 500 grams of "nutrose" (sodiocasein), the whole being then allowed to remain at 35° for 8 days; most of the tyrosine separated in the interval. The liquid was then exactly neutralised with hydrochloric acid, filtered, and concentrated, when the rest of the tyrosine separated first, and then the leucine. The latter was purified by freezing the aqueous solution of its hydrochloride, filtering it at a low temperature, and boiling the crystals with 3—4 per cent. ethyl-alcoholic hydrogen chloride, by which means the *hydrochloride* of the *ethylic salt*, $HCl,NH_2\cdot C_5H_{10}\cdot COOEt$, was obtained. This melts at 134°, and in 5 per cent. alcoholic solution has the rotation $[\alpha]_D = +18·4°$. If it is heated in aqueous solution at 200° for several days, the rotation attains a minimum, and a leucine hydrochloride is obtained which yields an ethylic salt melting at 112°, and was found to be identical with leucine prepared from a sample of commercial valeraldehyde (isovaleraldehyde?) that boiled at 92—95°, and had a rotation $\alpha = +38'$ in a 2 dm. tube. By treatment with sodium nitrite and sulphuric acid, the crude leucine was converted into a leucic acid, $OH\cdot C_5H_{10}\cdot COOH$, which melted at 78°, and had a rotation $[\alpha]_D = -7·6°$; inactive leucic acid, prepared from the inactive leucine, melted at 74°. C. F. B.

Organic Chemistry.

Californian Petroleum. By Charles F. Mabery (*Amer. Chem. J.*, 1897, 19, 796—804).—This paper contains a preliminary account of experiments on the composition of Californian petroleum. The samples examined differ markedly; one from Ventura County, which is very thick and nearly black, is a highly sulphurised oil (0·84 per cent.), and contains a large amount of nitrogen (0·53 per cent.). It unites with more bromine (17·72 per cent.) than Pennsylvanian or Ohio oils, but approximately the same as Canadian oil; probably a considerable portion of the bromine disappears by substitution, since the crude oil contains a large amount of aromatic hydrocarbons. In the lower fractions, the hydrocarbons belong to the series C_nH_{2n}.

Fresno County petroleum is lighter in colour than the foregoing, and has more of a greenish hue. It contains 0·21 per cent. of sulphur, and gave a bromine absorption of 9·07 per cent. A. W. C.

Constitution of Inorganic Compounds, X. Ammoniacal Chromiumthiocyanogen Compounds, By Alfred Werner and Georg Richter (*Zeit. anorg. Chem.*, 1897, 15, 243—277).—The authors have examined the two salts known as Reinecke's and Morland's salts which are formed by the action of potassium dichromate on fused ammonium thiocyanate, a mixture of the two salts being obtained by gradually adding the powdered dichromate (40 grams) to fused ammonium thiocyanate (200 grams); the powdered melt is treated with a small quantity of cold water, and the residue, which contains the two salts together with sulphur, is extracted with successive quantities of water at 50° with the addition of a few drops of acetic acid as long as considerable quantities of Reinecke's salt are removed, Morland's salt remaining undissolved.

Reinecke's salt, or, according to Werner's nomenclature, *potassium tetrathiocyanodiamminechromium*, $KCr(NH_3)_2(SCN)_4,H_2O$, is prepared from the above aqueous extract, in which it is mixed with the ammonium salt, by precipitating it as cadmium salt and decomposing the latter by an aqueous solution of potassium hydrogen sulphide. It crystallises in ruby-red, lustrous plates, or, without water of crystallisation, in scarlet nodules or rhombododecahedra. A determination of the number of ions in the aqueous solutions shows that the salt is easily split into the two ions $Cr(NH_3)_2(SCN)_4$ and K.

From the residue, obtained as mentioned above, Morland's salt is extracted by hot water containing a few drops of acetic acid; it cannot, however, be completely separated from the preceding salt, either by crystallisation from water or from alcohol. When it is converted into the cadmium salt, and the latter is decomposed by a solution of potassium hydrogen sulphate, it yields Reinecke's salt, and the filtrate from the cadmium salt contains guanidine. It is therefore *guanidine tetrathiocyanodiamminechromium.*

Nitrosyl tetrathiocyanodiamminechromium, $Cr(NH_3)_2(SCN)_4NO$, may

be prepared by adding to a saturated solution of Reinecke's salt, 10 per cent. of its volume of dilute nitric acid (1 acid to 1 water). It is also obtained by treating an acidified solution of Reinecke's salt with nitric peroxide, or, better, with a mixture of nitric oxide and nitrous oxide, or with a nitrite; in the last two cases, a quantitative precipitation is obtained. The crystalline precipitate is washed with water containing a few drops of nitric acid and dried on a porous plate. It crystallises in right-angled, four-sided prisms which are dark reddish-brown by transmitted light; the small crystals are dark brown in reflected light, the larger ones black. It is decomposed by water with partial oxidation into Reinecke's acid. With alkalis, it yields Reinecke's salt and a nitrite; with ammonia, Reinecke's ammonium salt with violent evolution of nitrogen. By careful oxidation with nitric acid, it yields the compound $Cr(NH_3)_2(SCN)_3(H_2O)_2$.

a-Trithiocyanodiaquodiamminechromium, $Cr(NH_3)_2(SCN)_3(H_2O)_2$, has already been obtained by Nordenskjöld (*Zeit. anorg. Chem.*, 1, 137) by oxidising Reinecke's salt with hydrogen peroxide. It is also obtained by the electrolysis of a solution of Reinecke's salt, by oxidising it with potassium chlorate and hydrochloric acid, and by cautious oxidation with warm dilute nitric acid. It is most easily obtained by acting on Reinecke's salt (10 grams) with a concentrated solution of hydrogen peroxide prepared by treating sodium peroxide (10 grams) with a slight excess of concentrated hydrochloric acid and twice its volume of ice; as soon as the violent evolution of hydrogen cyanide commences, the mixture is cooled sufficiently to maintain the temperature below 70—80°. The mixture is then filtered and the filtrate evaporated at the ordinary temperature until salt commences to separate, when the whole of the trithiocyanodiaquodiamminechromium will have crystallised out; finally, the product is purified by crystallisation from alcohol. When dissolved in water, no ionisation takes place. When treated with ammonia, a mixture of compounds containing more ammonia is obtained, but these have not yet been separated.

β-trithiocyanodiaquodiamminechromium, isomeric with the preceding compound, is obtained along with the preceding salt by the oxidation of Reinecke's salt or the compound $Cr(NH_3)_2(SCN)_4NO$ with nitric acid at 100°. It can be separated from its isomeride by crystallisation from warm water, in which it is less soluble. The α-trithiocyanide crystallises in six-sided tablets with an angle of 120° belonging to the hexagonal system; the β-trithiocyanide in four-sided tablets with angles of 104° and 76°, belonging to the monosymmetric system. The α-compound has a more intense and bluish-red colour; the β-compound is yellowish-red; both compounds when warmed with a concentrated solution of alkali thiocyanate at 100° are at once converted into Reinecke's salt. The two compounds give precipitates with many salts of the heavy metals and with organic bases containing nitrogen, a list being given of those which can be used to distinguish between the isomerides. For example, with cadmium chloride, a 5 per cent. aqueous solution of the α-compound yields a bright red precipitate, the β-compound no precipitate; with guanidine nitrate, the α-compound yields a very characteristic precipitate of elliptical leaflets, the β-compound no precipitate. E. C. R.

Action of Nitric Acid on Potassium Cobalticyanide. By ÉMILE C. A. FLEURENT (*Compt. rend.*, 1897, **125**, 537—538).—When 100 parts of potassium cobalticyanide is heated at 100° for about 10 hours with 500 parts of nitric acid diluted with an equal volume of water, a deep orange-red, fluorescent liquid is obtained, and if after separation of the potassium nitrate by crystallisation this is neutralised with potassium carbonate and mixed with excess of alcohol of 66°, the syrupy mass described by Jackson and Comey (Abstr., 1896, i, 402) separates, but the liquid also contains a product which gives all the reactions of nitroprussides and is most readily separated in the form of the cupric salt. C. H. B.

Hydrates of Magnesium Platinocyanide and their Solubility. By HELLMUTH (BARON) BUXHOEVDEN and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1897, **15**, 319—327).—Magnesium platinocyanide is obtained by decomposing the copper salt, suspended in water, with hydrogen sulphide, neutralising the solution of hydrogen platinocyanide thus formed with magnesia, evaporating, and allowing it to crystallise. The red crystals thus obtained always contain less water than is required by the formula $MgPt(CN)_4 + 7H_2O$. The vapour tension of a saturated solution at 19° of the composition $MgPt(CN)_4 + 37·2H_2O$ is 14·4 mm.; when the vapour tension is greater, the crystals deliquesce, and at a lower vapour tension they give off water, whilst at a pressure of 7 mm. the yellow hydrate with $5H_2O$ is formed. Homogeneous red crystals with 6·8—6·25 H_2O are obtained at 19° under a vapour tension of 14·4—7 mm. Neither the hydrate with $7H_2O$ nor the hydrate with $6H_2O$ crystallises from the saturated solution, but from 0—45° crystals with 6·9—6·6 H_2O are obtained; the vapour tension of these crystals is the same as that of the solutions from which they are obtained. When these red crystals are dried, the following hydrates are obtained: at 45°, a bright yellow hydrate with $5H_2O$; at 60°, a bright green hydrate with $4H_2O$; at 100°, a white hydrate with $2H_2O$, and at 210°, the orange-red, anhydrous salt. These hydrates are present in the saturated solutions as follows, from −4·12—45° the red hydrate, above 45° the hydrate with $5H_2O$ is formed, from 45—88° the green hydrate is stable, and above 88° the white hydrate is formed.

Tables and curves of the solubility of the various hydrates are given. The results show that each hydrate has a characteristic solubility. E. C. R.

Synthesis of Hexamethylene-glycol Diethyl Ether and other Ethers from Trimethylene Glycol. By ARTHUR A. NOYES (*Amer. Chem. J.*, 1897, **19**, 766—781).—*Trimethyleneglycol monethylic ether*, produced by the action of ethylic iodide on the monosodium derivative of trimethylene glycol, is a colourless, pleasant-smelling liquid, miscible with water in all proportions; it boils at 160—161° (corr.), has a sp. gr. = 0·915 at 25°/25°, and an index of refraction 1·416 at 25°.

[With H. M. CHASE.]—The corresponding *diethylic ether*, which is a liquid insoluble in water, possesses a fruity odour, boils at 140—141° (corr.), and has sp. gr. = 0·835 at 25°/25°.

Ethylic γ-chlorpropylic ether, prepared by the action of phosphorus

trichloride on the above monethylic ether, is a liquid boiling at 130—131° (corr.) and of sp. gr. = 0·957 at 25°/25°. The corresponding *bromo*-compound is an aromatic-smelling liquid, insoluble in water, boiling at 150—151°, and having a sp. gr. = 1·3 at 25°/25°.

[With Grace A. Van Everen] the *iodo*-compound boils at 130—134° (150 mm.), and has a sp. gr. = 1·585 at 25°/25°.

Hexamethylene glycol diethylic ether is obtained by the action of sodium on ethylic γ-chloro- (bromo- or iodo-) propylic ether, the best yield (28—30 per cent.) being obtained with either the bromo- or iodo-compounds. It is a colourless liquid, insoluble in water, boiling at 208° (corr.) at ordinary atmospheric pressure, and having a sp. gr. = 0·846 at 25°/25°; it dissolves in cold concentrated sulphuric acid, and is reprecipitated on adding water. Phosphorus trichloride has little or no action on it.

[With L. H. Goodhue.]—γ-*Ethoxybutyric acid*,

$$OEt\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH,$$

was prepared by the action of potassium cyanide on ethylic γ-bromopropylic ether, and subsequent hydrolysis of the nitrile thus obtained; it is a colourless liquid, soluble in water, and boils between 230—240°. On submitting the potassium salt of this acid to electrolysis, small amounts of hexamethylene-glycol diethylic ether were obtained.

[With H. H. Tozier.]—*Ethylic γ-phenylpropylic ether*, prepared by the action of sodium on a mixture of bromobenzene and ethylic bromopropylic ether, is a liquid of terpene-like odour, boiling at 224° (corr.), and having a sp. gr. = 0·924 at 15°/15°.

[With C. H. Stone.]—*Ethylic γ-ethoxypropylmalonate*, obtained by the action of ethylic bromopropylic ether on ethylic sodiomalonate, is a nearly odourless liquid boiling at 273° (corr.) and of sp. gr. = 1·016 at 15°/15°. On hydrolysis and subsequent elimination of carbonic anhydride from the dicarboxylic acid, δ-*ethoxyvaleric acid* is obtained as a colourless liquid, soluble in water, boiling at 252°, and having a sp. gr. = 0·994 at 25°/25°. Another substance was produced in this reaction, but its exact nature was not determined. A. W. C.

Formaldehyde Derivatives of the Polyatomic Alcohols and Acids of the Sugar Group. By K. Weber and Bernhard Tollens (*Ber.*, 1897, **30**, 2510—2514. Compare Abstr., 1894, i, 438; 1896, i, 645).—With formaldehyde and hydrochloric acid, dulcitol yields *dimethylenedulcitol*, $C_6H_{10}(CH_2)_2O_6$, which is optically inactive and crystallises in needles melting at 244—245°; the *dibenzoate* $C_6H_8O_4(CH_2)_2(OBz)_2$, melts at 228—231°, and the *diacetate* at 258—260°. *Dimethylenerhamnitol*, $C_6H_{10}(CH_2)_2O_5$, is prepared from rhamnitol and crystallises in needles melting at 138—139°. It is dextrorotatory, $[\alpha]_D = +9°$; the *monobenzoate* forms needles, which melt at 136—137°. *Monomethylenerhamnonic lactone*, $C_6H_8O_5\colon CH_2$, is obtained from rhamnonic lactone and crystallises in tablets which melt at 178—180°; it is lævorotatory ($[\alpha]_D = -85·4°$) and is monobasic towards warm aqueous soda.

Rhamnohexonic acid does not yield any formaldehyde derivative; glucoheptonic lactone, on the other hand, is readily converted into *dimethyleneglucoheptonic lactone*, $C_7H_8(CH_2)_2O_7$, which has been ob-

tained in two different forms; the less soluble of these is lævorotatory ($[\alpha]_D = -69.5°$) and melts at about 280°, whereas the more soluble has a greater rotation ($[\alpha]_D = -101°$) and melts at about 230°. The acid is readily decomposed by bases, and hence it is extremely difficult to prepare its salts. When saccharin is treated with formaldehyde and hydrochloric acid, a substance is formed which has the composition of *trimethylenedisaccharin*, $C_{12}H_{14}(CH_2)_3O_{10}$, crystallises in needles or plates, melts at 139—140°, and is lævorotatory; $[\alpha]_D = -22.8°$. The presence of the carboxyl group appears to hinder the action of formaldehyde with the adjacent hydroxyl group, the action being further influenced by the configuration of the reacting substance. It appears that substances which yield mucic acid react much less completely than their isomerides; thus mucic acid itself gives no formaldehyde, and the same is true of rhamnohexonic acid, which yields mucic acid on oxidation. Moreover, dulcitol only yields a dimethylene-derivative, whilst its isomerides, mannitol and sorbitol, form trimethylene compounds. A. H.

Preparation of Soluble Starch and Starch Solution. By OTTO FOERSTER (*Chem. Zeit.*, 1897, 21, 41).—To prepare soluble starch, a paste of 20 to 25 grams of starch with water is poured in a thin stream into 200 to 300 c.c. of hot water containing 5 c.c. of concentrated hydrochloric acid, the liquid being stirred until it becomes homogeneous and fairly fluid; heat is then applied and the stirring continued until the liquid is clear and as limpid as water. After cooling, it is filtered, alcohol added to the filtrate, the precipitate which is formed washed with alcohol until free from chlorine, then with ether, allowed to dry in the air, and finally dried by gently warming, or, better, by allowing it to remain over sulphuric acid. To prepare a solution of starch, 20 grams are dissolved as described above, the hydrochloric acid being carefully measured so that it may afterwards be exactly neutralised. The volume of the neutral filtered solution is made up to a litre by adding glycerol. The excess of water can be evaporated after the addition of the glycerol, whereby the stability of the solution is perhaps increased. Both these preparations give blue colorations with iodine. E. W. W.

Soluble Starch. By WIKTOR SYNIEWSKI (*Ber.*, 1897, 30, 2415—2418).—Soluble starch may be obtained by the action of a 9 per cent. solution of sodium peroxide on potato starch suspended in water, and is purified by repeated precipitation by alcohol, when it forms a snow-white, amorphous substance which is almost free from ash; this has the composition $3C_6H_{10}O_5 + H_2O$, is soluble to the extent of 12·5 per cent. in cold water, and in all proportions in hot water; the aqueous solution is not altered by warming on the water bath, and is coloured a pure blue by iodine. The compound is dextrorotatory, but the specific rotation increases with the concentration of the solution. The yield is about 90 per cent. of the original material, the loss being purely mechanical. (Compare Wróblewski, this vol., i, 8.) A. H.

Bromethylamine and Vinylamine. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, 30, 2494—2497).—Sodium hydrogen

carbonate may be used instead of silver carbonate to convert bromethylamine hydrobromide into hydroxyethylcarbamic anhydride (Abstr., 1888, 439), the two substances being warmed together at 40—60°. The anhydride, when boiled with aniline, yields ethylenephenylcarbamide, $\begin{matrix} CH_2\cdot NPh \\ | \\ CH_2\cdot NH \end{matrix}\!\!>\!CO$. Bromethylamine hydrobromide can be converted, with satisfactory yield, into μ-methyloxazoline (Abstr., 1889, 1134) by boiling it with acetic anhydride for 3 hours, distilling off the excess of the anhydride at 60° under diminished pressure, diluting the residue with water, adding excess of potassium hydroxide, cooling meanwhile, and then distilling with steam; μ-methyloxazoline boils at 109·5—110·5°, and its picrate is now found to melt at 159—160°; the lemon-yellow *aurochloride* melts at 184—185°.

Vinylamine reacts with hydrogen sulphide, yielding thioethylamine (Abstr., 1891, 816). C. F. B.

Rapid Polymerisation of Chloral. By JOHN W. MALLET (*Amer. Chem. J.*, 1897, **19**, 809—810).—A specimen of anhydrous chloral, contained in a glass vial with small, drawn-out neck hermetically sealed, polymerised so rapidly as to cause the bursting of the vial. The occurrence is remarkable, inasmuch as the amount of heat evolved in the polymeric change must have been sufficient to produce the effect observed; also the polymeric change must have occurred with a suddenness which is surprising in view of the very gradual transition of liquid chloral into meta-chloral; and it is not easy to imagine what caused the sudden polymerisation, there having been less change of temperature or external disturbance of any kind, at the time when the change occurred, than the specimen had been previously exposed to.

A. W. C.

Glyoxalosazone from Formaldehyde. By HANS VON PECHMANN (*Ber.*, 1897, **30**, 2459—2461).—Five compounds have already been isolated from the product of the action of phenylhydrazone on formaldehyde, and in the present paper a sixth is described, which is formed when the reaction takes place in acetic acid solution and the concentration and temperature are so arranged that the liquid remains clear at first. The substance thus formed is identical with glyoxalosazone, and is probably formed by the aldehyde undergoing an aldol condensation, either through the hydrazine or the acetic acid, with formation of glycolaldehyde.

Glyoxalosotetrazone which has been previously described as an oil, crystallises from acetone or alcohol in characteristic, dark-red plates melting at 152°. J. F. T.

Change of Butyric into Isobutyric Acid. By RUDOLF HUTZLER and VICTOR MEYER (*Ber.*, 1897, **30**, 2519—2529).—Erlenmeyer (*Annalen*, 1876, **181**, 126) found that a tube containing a cold saturated solution of calcium butyrate which had been used to show the separation of the salt at 100°, remained clear at this temperature after about 10 years' use. By fractional crystallisation of the contents of the tube, he isolated a salt which he regarded as calcium isobutyrate, and which comprised about $\frac{1}{12}$—$\frac{1}{10}$ of the whole amount of salt present.

The authors have found that this proportion of isobutyrate cannot be detected in this way in a mixture of the two isomeric salts. A trustworthy method for detecting this amount of isobutyrate is to submit the mixture to oxidation with potassium permanganate. The normal acid is chiefly converted into carbonic anhydride, whereas the iso-acid yields acetonic acid. Experiments were then made with tubes of resistant glass containing sterile solutions of pure calcium butyrate, and it was found that, after being heated for 6 months at 100°, they no longer gave a precipitate on heating. Isobutyric acid could not be detected in their contents, and the cause of the change was found to be the conversion of a small proportion of the calcium butyrate into the potassium salt by potassium silicate from the glass, calcium silicate being precipitated. The amount of calcium salt is thus diminished to such an extent that the liquid is not saturated at 100°, and hence no precipitation occurs.

A. H.

Conversion of Pentachloracetone into Trichloracrylic Acid and Chloromalonic Acid. By PAUL FRITSCH (*Annalen*, 1897, **297**, 312—322. Compare Abstr., 1894, i, 490).—*Heptachloropropane*, $CHCl_2\cdot CCl_2\cdot CCl_3$, is obtained by heating pentachloracetone with phosphorus pentachloride in a sealed tube at 180° during 6—8 hours; it has the odour of camphor, melts at 30°, boils at 150—151° under a pressure of 50 mm., and at 247—248° under atmospheric pressure, slight evolution of hydrogen chloride occurring at that temperature.

Hexachloropropylene, $CCl_2{:}CCl\cdot CCl_3$, prepared from the foregoing substance by the action of alcoholic potash (1 mol.), is an oil which has an odour of raspberries. It has a sp. gr. = 1·7652 at 20°/4°, and the refractive index $n_D = 1\cdot5091$; it boils at 122—123° under a pressure of 50 mm., and at 209—210° under atmospheric pressure.

Ethylic orthotrichloracrylate, $CCl_2{:}CCl\cdot C(OEt)_3$, is produced when hexachloropropylene is treated with a slight excess of sodium ethoxide; it has a sp. gr. = 1·2183 at 20°/4°, and the refractive index $n_D = 1\cdot4649$. It boils at 149° under a pressure of 50 mm., and at 236—237° under atmospheric pressure.

Ethylic trichloracrylate, $CCl_2{:}CCl\cdot COOEt$, obtained by agitating ethylic orthotrichloracrylate with concentrated hydrochloric acid, is a colourless oil having the odour of peppermint, and boils at 112—114° under a pressure of 50 mm., and at 192—194° under atmospheric pressure; its sp. gr. = 1·3740 at 20°/4°, and the refractive index $n_D = 1\cdot4839$. The *anhydride* of trichloracrylic acid is insoluble in water, and melts at 39—40°, whilst the *amide* crystallises from water in colourless needles, and melts at 96—97°; the *carbamide* forms stellar aggregates of needles, and melts at 165°.

Ethylic α-chloro-β-diethoxyacrylate, $C(OEt)_2{:}CCl\cdot COOEt$, formed from ethylic trichloracrylate by the action of sodium ethoxide, boils at 157—159° under a pressure of 50 mm., and at 226—230° under atmospheric pressure; it has a sp. gr. = 1·0843 at 20°/4°, and the refractive index $n_D = 1\cdot4319$. Agitation with concentrated hydrochloric acid converts the ethereal salt into ethylic monochlormalonate.

M. O. F.

Reaction between Ethylic Isonitrosoacetoacetate and Hydroxylamine Hydrochloride. By MILORAD Z. JOVITSCHITSCH (*Ber.*, 1897, **30**, 2421—2422. Compare Abstr., 1896, i, 81).—The yield of oximidomethylisoxazolone may be increased by extracting with ether the mother liquor left after the separation of the compound. If after this treatment it be neutralised with sodium carbonate, a precipitate is obtained, which consists of the compound first prepared by Scholl from isonitrosoacetone and hydroxylamine. A. H.

Colour Reactions of Pyruvic Acid. By LOUIS SIMON (*Compt. rend.*, 1897, **125**, 534—536).—When a solution of pyruvic acid is mixed with potassium hydroxide and then with sodium nitroprusside, an intense violet-red coloration is produced, which is turned red by a small quantity of acetic acid, but decolorised by an excess. This reaction is not, however, characteristic, but is shown by a large number of aldehydes, ketones, and their derivatives and condensation products.

On the other hand, if ammonia is substituted for the potassium hydroxide in the foregoing reaction, pyruvic acid gives a beautiful, violet-blue coloration, which is characteristic of pyruvic acid and its metallic and ethereal salts, but does not seem to be given by any other compound except acetophenone, and this is readily distinguished from pyruvic acid by Legal's reaction. A small quantity of acetic acid, but not sufficient to make the liquid acid, is essential to the production of the blue colour, and under these conditions the limit of the reaction seems to be reached when the solution contains 1 part of pyruvic acid in 10,000. In the absence of acetic acid, the coloration is green, not blue, and the limit is reached with 1 part of acid in 5,000 of water. The coloration appears gradually, and its appearance is accelerated by gently heating, but the colour is destroyed by boiling, and also by an excess of acetic acid. Potassium hydroxide changes the blue to deep-red, but addition of acetic acid restores the blue.

When amines of the acetic series are added to a solution of pyruvic acid mixed with sodium nitroprusside, a deep-violet coloration rapidly appears and then rapidly disappears; it is changed to blue by acetic acid, but the blue likewise rapidly disappears. All the amines of the acetic series seem to give this reaction. C. H. B.

[Beryllium Oxalates.] By ARTHUR ROSENHEIM and PAUL WOGE (*Zeit. anorg. Chem.*, 1897, **15**, 283—318).—See this vol., ii, 71.

A New Double Platinum Salt. By MAURICE VÈZES (*Compt. rend.*, 1897, **125**, 525—527).—When a solution of oxalic acid is added, in rather more than equal molecular proportion, to a hot concentrated solution of potassium platonitrite, the liquid becomes green, and nitrogen oxides are liberated; after a time, however, the liquid becomes golden-yellow, and when cooled yields pale-yellow, prismatic crystals which act on polarised light. These consist of potassium plato-oxalonitrite, and have the composition $K_2PtC_2O_4(NO_2)_2 + H_2O_2$. They are stable in air, lose their water of crystallisation above 100°, and at about 240° decompose completely, with intumescence, into platinum, potassium nitrite, and carbonic anhydride. The salt is very slightly soluble in

cold water, but somewhat soluble in boiling water, and is very stable in solution.

When an excess of oxalic acid is used in the reaction described, the product is the potassium platoxalate, $K_2PtC_2O_4 = 2H_2O$, which crystallises in copper-red needles, and was described by Söderbaum (Abstr., 1886, 532). When the platinum salt is in excess, there is no formation of any intermediate compound analogous to the halogen compounds of the type $K_2PtX(NO_2)_3$ previously described by the author.

The author suggests that when platinum is separated from associated metals in the form of potassium platonitrite, the readiest method of isolating it is to precipitate it as plato-oxalonitrite, and afterwards decompose the latter by heat. C. H. B.

The Isomeric Ethylic Diacetylsuccinates. By LUDWIG KNORR (*Ber.*, 1897, **30**, 2387—2389).—The details of the work which is summarised in this preliminary communication will shortly appear in the *Annalen*. The author has succeeded in obtaining no less than five isomerides of ethylic diacetylsuccinate. Three of these are enol-forms (α_1, α_2, and α_3), which probably have the configurations

$$\begin{array}{c}\text{Me·C·OH}\\ \|\\ \text{COOEt·C·C·COOEt}\\ \|\\ \text{HO·C·Me}\end{array}\qquad\begin{array}{c}\text{HO·C·Me}\\ \|\\ \text{COOEt·C·C·COOEt}\\ \|\\ \text{Me·C·OH}\end{array}\qquad\begin{array}{c}\text{Me·C·OH}\\ \|\\ \text{COOEt·C·C·COOEt}\\ \|\\ \text{Me·C·OH}\end{array}$$

The remaining two are the optically inactive keto-forms (β and γ). Neither of these has yet been resolved into optically active constituents. The following table exhibits the chief properties of these isomerides :

	Melting point.	Index of refraction.	Ferric chloride coloration.	Solubility in light petroleum at 20° (b. p. 50—60°).
β	89°	—	—	1 : 122·5
γ	68°	—	—	1 : 15·3
α_1	liquid	1·5900	brown	1 : 9·7
α_2	21—22°	1·4530	violet	every proportion
α_3	31—32°	1·4392	—	1 : 2·9

The enol-forms have all a faintly acid reaction, and are soluble in aqueous sodium carbonate, but readily become ketonised in this solution. All five isomerides yield the same products when submitted to various chemical reactions.

They are all unstable in the liquid state and in solution, and hence, under these conditions, a state of equilibrium is attained in which the proportions of the various isomerides present can be experimentally determined for different temperatures.

The author considers that the passage of one isomeride into the other is brought about by the migration of the mobile hydrogen atoms. It seems probable, in the light of these results, that liquid tautomeric substances are usually mixtures of the various desmotropic forms of the compound. Solid tautomeric substances, on the other hand, usually represent one definite form. A. H.

Compound of Titanic Acid with Malic Acid. By Georg Berg (*Zeit. anorg. Chem.*, 1897, **15**, 328—330).—The following organic acids do not cause a precipitate in neutral solutions of titanium chloride—malonic, succinic, citric, fumaric, maleic, amidosuccinic, benzoic, orthohydroxybenzoic, benzenedisulphonic, phenylacetic, meta- and para-amidobenzoic, hippuric, phthalic, hydroxybutyric, and crotonic, also phenol, trinitrophenol, and resorcinol. White, amorphous precipitates are obtained with acetic, lactic, tribromolactic, tribromacetic, and ψ-cumenesulphonic acids. A reddish-brown precipitate is produced by nitroso-β-naphthol, a yellow with salicylic acid, and a yellowish-brown with potassium chromate.

Malic acid (also its salts) is the only compound examined which gives a crystalline precipitate; the latter, $2TiO_2,C_4H_6O_5 + 6H_2O$, crystallises in minute, white prisms, is very stable, and is only slowly decomposed by boiling with water or barium hydroxide solution. It is very sparingly soluble in water, strong acetic acid, or dilute mineral acids, but less so in alcohol. It dissolves slowly in concentrated sulphuric and nitric acids, and at once in concentrated hydrochloric acid. It dissolves at once in caustic alkalis with precipitation of titanic acid, more slowly in ammonia and alkali carbonates. When the crystals are treated with ammonia, they lose $3H_2O$ and take up $3NH_3$, and if this compound is allowed to remain exposed to the air it gives off ammonia, and is converted into the compound $2TiO_2,C_4H_6O_5,2NH_3 + 3H_2O$.

Malic acid cannot be employed for the separation of titanic acid from zirconium or iron, as the last two are also precipitated.

E. C. R.

Compounds of Formaldehyde with Uric Acid. By K. Weber, R. Pott, and Bernhard Tollens (*Ber.*, 1897, **30**, 2514—2515).—Diformaldehyde-uric acid, $C_5H_4N_4O_3 + 2CH_2O$, is readily formed, and is monobasic towards one-third normal soda. The mother liquor from its preparation, when treated with alcohol and ether, yields a substance which appears to contain 4—5 mols. of formaldehyde to 1 of uric acid.

A. H.

Aliphatic Derivatives of Hydroxythiocarbamide. By Carl Kjellin and K. Gustav Kuylenstjerna (*Annalen*, 1897, **298**, 117—129. Compare Tiemann, Abstr., 1889, 1165, and Voltmer, Abstr., 1891, 558).—*Hydroxyethylthiocarbamide*, NHEt·CS·NH·OH, is obtained by carefully adding an ethereal solution of hydroxylamine to ethylthiocarbimide dissolved in the same medium; it forms colourless needles or prisms, explodes slightly when touched with a hot glass rod, and melts and decomposes at 109°. The dry substance begins to undergo decomposition after about a week, yielding a mixture of sulphur and ethylcarbamide, but the aqueous and alcoholic solutions are very unstable, precipitation of sulphur occurring in a few minutes; silver and copper sulphides are produced by the action of silver nitrate and Fehling's solutions. Ferric chloride develops an olive-green coloration with the alcoholic solution, whilst the aqueous solution becomes violet; both colours, however, disappear rapidly.

Hydroxymethylthiocarbamide, NHMe·CS·NH·OH, which crystallises in small, colourless, six-sided plates, sinters at 95°, and explodes at

101°; it closely resembles the foregoing compound, and is considerably less stable than that substance.

Hydroxyallylthiocarbamide, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot OH$, crystallises in microscopic, rectangular plates, forming a colourless, nacreous precipitate when ethereal allylthiocarbimide is added to anhydrous hydroxylamine dissolved in the same medium; it begins to soften at 85°, and fuses completely at 120°. It is extremely unstable, both in the solid state and in solution, yielding sulphur and allylcarbamide; the colour changes with ferric chloride are the same as those exhibited by hydroxyethylthiocarbamide and hydroxymethylthiocarbamide.

Symmetrical hydroxydiethylthiocarbamide, $NHEt\cdot CS\cdot NEt\cdot OH$, is prepared by treating an ethereal solution of β-ethylhydroxylamine with ethereal ethylthiocarbimide; it melts at 81°, dissolves sparingly in water and ether, and is readily soluble in alcohol, chloroform, and hot benzene. The crystals from benzene are monosymmetric; $a:b:c = 2\cdot8676:1:0\cdot8809$. $\beta = 86° 5'$. Hydroxydiethylthiocarbamide may be preserved for any length of time without undergoing change, and the aqueous solution does not yield sulphur when boiled; ferric chloride develops a green coloration with the aqueous or alcoholic solution, passing into bluish-green and reddish-violet on dilution. The *silver* derivative forms slender, silky needles containing $3H_2O$, and resists the action of light; the *gold chloride* derivative is red.

Symmetrical hydroxydimethylthiocarbamide, $NHMe\cdot CS\cdot NMe\cdot OH$, is prepared by adding the calculated amount of sodium methoxide dissolved in methylic alcohol to a solution of β-methylhydroxylamine hydrochloride and methylthiocarbimide in methylic alcohol; it separates from benzene in dimorphous crystals melting at 104°. The colour changes with ferric chloride are similar to those of the foregoing compound. The *silver* derivative forms slender, colourless needles, the *mercurichloride* is dimorphous, and the *aurochloride* is decomposed by water. Ethylic iodide converts hydroxydimethylthiocarbamide into an unstable crystalline compound, which yields ethyl mercaptan when heated with caustic soda.

Hydroxyethylallylthiocarbamide, $C_3H_5\cdot NH\cdot CS\cdot NEt\cdot OH$, obtained from β-ethylhydroxylamine and allylthiocarbimide, crystallises from benzene in thin, four-sided plates, and melts at 66—67°.

Hydroxymethylallylthiocarbamide, $C_3H_5\cdot NH\cdot CS\cdot NMe\cdot OH$, is prepared from β-methylhydroxylamine and allylthiocarbimide; it melts at 54°, and crystallises from benzene in beautiful, colourless, monosymmetric prisms. $a:b = 0\cdot60264:1$. $\beta = 74° 8'$.

Hydroxymethylethylthiocarbamide, $NHMe\cdot CS\cdot NEt\cdot OH$, obtained from β-ethylhydroxylamine and methylthiocarbimide, crystallises in small, colourless needles, and melts at 122° when heated rapidly.

Benzyloxyallylthiocarbamide, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot O\cdot CH_2Ph$, is prepared from β-benzylhydroxylamine and allylthiocarbimide; it forms prismatic crystals and melts at 57—58°. M. O. F.

Polyaspartic Acids. By HUGO SCHIFF (*Ber.*, 1897, **30**, 2449—2459).—The two anhydrides of aspartic acid prepared by Schaal by the action of carbonic anhydride on asparagine are more easily prepared by heating aspartic acid at 190—200° for 20 hours;

on boiling the product with ten times its weight of water the octo-anhydride (*octoaspartide*), $C_{32}H_{26}N_8O_{17}$, remains undissolved, whilst the tetra-anhydride (*tetraspartide*), $C_{16}H_{14}N_4O_9$, separates from the filtrate on cooling. The filtrate also contains two other substances, namely, *tetraspartic acid*, $C_{16}H_{22}N_4O_{13}$, and a small quantity of *octo-aspartic acid*, $C_{32}H_{42}N_8O_{25}$, the latter can also be obtained from its copper salt by treatment with hydrogen sulphide; it forms a vitreous mass which at 190—200° passes quantitatively into octoaspartide. Octoaspartide combines with 8 mols. of phenylhydrazine with the formation of a yellow, crystalline *phenylhydrazide*, melting partially and decomposing at 200—205°. It also combines with aniline with the production of various products, those containing less than 8 mols. of aniline dissolving in alkali with the formation of the corresponding octoaspartanilic acids; on heating with aniline, ammonia is evolved.

Tetraspartic acid crystallises from water in clusters of needles, and is very similar to the octo-acid in its properties.

The author considers the constitution of octoaspartic acid and tetr-aspartic acid to be respectively

$$HO\left(CO\cdot\overset{NH_2}{\overset{|}{\underset{|}{C}}}\cdot CH_2\cdot COOH\right)_8H \quad \text{and} \quad HO\left(CO\cdot\overset{NH_2}{\overset{|}{\underset{|}{C}}}\cdot CH_2\cdot COOH\right)_4H,$$

and that of tetraspartide and octoaspartide to be

$$HO\left(\cdot CO\cdot\overset{NH\text{——}}{\overset{|}{\underset{|}{C}}}\cdot CH_2\overset{|}{C}O\right)_4H \quad \text{and} \quad HO\left(\cdot CO\cdot\overset{NH\text{——}}{\overset{|}{\underset{|}{C}}}\cdot CH_2\overset{|}{C}O\right)_8H.$$

J. F. T.

Aliphatic Sulphonic Acids. By ELMER P. KOHLER (*Amer. Chem. J.*, 1897, **19**, 728—752).—From the study of the behaviour of some 23 sulphonic acids towards phosphorus pentachloride, and of the corresponding chlorides towards water, the details of which will appear in subsequent papers, the author is led to the following general conclusions, to which no exceptions have so far been observed.

Monosulphonic acids and *αα*-chloro- or bromo-monosubstitution products of monosulphonic acids react readily with phosphorus pentachloride in the cold with production of a normal sulphone chloride, which on treatment with water passes back into the acid.

With phosphorus pentachloride, 1 : 2-chloro- or bromo-sulphonic acid reacts in the same way; the chloride, on treatment with water, passes back for the most part into the acid, but at the same time an unsaturated sulphonic acid is formed,

$$CH_2Br\cdot CH_2\cdot SO_2Cl + H_2O = CH_2{:}CH\cdot SO_3H + HCl + HBr.$$

Neither *αα*- nor *αβ*-disulphonic acids react with phosphorus pentachloride in the cold. On heating, in the first case, the product is mainly an *αα*-chlorsulphonic chloride, together with other chlorine substitution products; and in the second case a disulphonic chloride is formed, which on treatment with water gives principally an unsaturated sulphonic acid, and to a minor extent the regenerated acid.

αα- and *αβ*-Sulphocarboxylic acids slowly react with phosphorus pentachloride in the cold. The product is always a chlorine substitution

product of a diacid chloride, which reacts with water in a complicated manner, with different results in different cases.

The special subject treated in this paper is the behaviour of $\alpha\beta$-ethanedisulphonic chloride towards a number of reagents in order to determine what conditions are most favourable for the production of an unsaturated acid, or the regeneration of the saturated acid.

$\alpha\beta$-Ethanedisulphonic acid is produced by the oxidation of ethylenic thiocyanate with nitric acid, and crystallises from glacial acetic acid in slender needles melting at 100°. The *sodium* salt is best obtained by boiling ethylenic dibromide and sodium sulphite in concentrated aqueous solution; if the solution is dilute, then sodium monobromethanesulphonate is produced.

$\alpha\beta$-Ethanedisulphonic chloride, prepared either from the free acid by treatment with phosphorus pentachloride or carbonyl chloride, or from the sodium salt of the acid by warming with phosphorus pentachloride, crystallises from chloroform in large, compact orthorhombic tables melting at 91°. When pure, it can be heated to 150° without a trace of decomposition, but at 160° sulphurous anhydride is slowly evolved and $\alpha\beta$-chlorethanesulphonic chloride distils over.

All attempts to prepare an unsymmetrical disulphonic chloride failed.

When ethanedisulphonic chloride is acted on by water, an amount of ethylenesulphonic acid corresponding with 90 per cent. of the original substance and 10 per cent. of $\alpha\beta$-ethanedisulphonic acid are produced.

Methylic, ethylic, propylic and amylic alcohols react with the sulphonic chloride in the same way as water; the amount of unsaturated acid formed diminishes, however, with the increase in the molecular weight of the alcohol. Acids and alkalis also react in the same manner.

Dry ammonia does not act on the sulphonic chloride with production of the corresponding amide, and in alcoholic solution ammonium ethanedisulphonate and anhydrotaurine are formed.

Substituted ammonias behave in a similar manner, aniline, for example, giving rise to anhydrophenyltaurine and *anilidoethanesulphoneanilide*, $NHPh\cdot CH_2\cdot CH_2\cdot SO_2\cdot NHPh$; the latter is an oil which can with difficulty be obtained in colourless plates melting at 75°. The *hydrochloride* crystallises from alcohol in long, colourless needles melting at 171°, and the *monacetyl* derivative melts at 152°.

Acetamide, and acid amides in general, act on the chloride in glacial acetic acid solution, producing mainly ammonium ethanesulphonate.

When the chloride is acted on by sodium acetate (or salts of organic acids in general), sulphurous anhydride is eliminated and 95 per cent. of the original substance is recovered in the form of the sodium salt of ethylenesulphonic acid, and the remainder as sodium ethanedisulphonate.

Zinc dust converts 53 per cent. of the chloride into the zinc salt of $\alpha\beta$-ethanedisulphinic acid, another substance not fully investigated being also produced. A. W. C.

Constitution of Meconic Acid. By ALBERTO PERATONER (*Chem. Zeit.*, 1897, **21**, 40).—Meconic acid, when boiled with alkalis or

alkaline earths, yields carbonic anhydride, oxalic acid, formic acid, and substances of a gummy nature whose isolation is rendered difficult by the presence of the acids. By the action of barium hydroxide on triethylic meconate, which was prepared by boiling the dry yellow trisilver salt with ethylic iodide and crystallising the product from light petroleum and ethylic alcohol, the author obtained barium oxalate, alcohol, and acetylcarbinylic ethylic ether, but neither carbonic nor formic acid. Since meconic acid belongs to the pyrone group as shown by its conversion into comenic acid (Ost) and since chelidonic acid, which is a pyronedicarboxylic acid, when treated with alkaline earths, splits up into oxalic acid and acetone, the above decomposition indicates the following formula for triethylic meconate $\begin{array}{l}COOEt{\cdot}C{-}O{-}C{\cdot}COOEt \\ \quad\;\; || \qquad\quad || \\ \quad\; CH{\cdot}CO{\cdot}COEt\end{array}$, and hence that the free acid is hydroxychelidonic acid. Similar experiments with pyromeconic acid show that this acid probably decomposes into formic acid and acetylcarbinol.

E. W. W.

Nitroketones, Hydroxyketones, Ketochlorides and Ketobromides. By E. C. THEODOR ZINCKE (*J. pr. Chem.*, 1897, [ii], **56**, 157—178).—This paper is chiefly theoretical in character, and contains no description of new compounds. By chlorinating tetrachloroparacresol in acetic acid solution, a ketochloride, $CMe{<}^{CCl\cdot CCl_2}_{CCl:CCl}{>}CO$, is obtained; at a higher temperature and without solvent, the isomeride, $CMeCl{<}^{CCl:CCl}_{CCl:CCl}{>}CO$. A ketobromide, $CMeBr{<}^{CCl:CCl}_{CCl:CCl}{>}CO$, analogous to the last compound, can be obtained in a similar way; it appears to exist only in this configuration, but it sometimes reacts as if it had the constitution $CH_2Br{\cdot}C{\lessgtr}^{CCl\cdot CCl}_{CCl:CCl}{\gtrless}C{\cdot}OH$. When oxidised with nitric acid, it yields a compound $OH{\cdot}CH_2{\cdot}CBr{<}^{CCl:CCl}_{CCl:CCl}{>}CO$; alkalis convert this into $\begin{array}{l}CH_2 \\ | \\ O{-}\end{array}{>}C{<}^{CCl:CCl}_{CCl:CCl}{>}CO$, whilst reduction changes it to $CMe{\lessgtr}^{CCl\cdot CCl}_{CCl:CCl}{\gtrless}C{\cdot}OH$. Many other reactions of these and similar substances are enumerated, and compared with similar ones observed by Auwers; it is not possible, however, to give a satisfactory abstract of them. It may be said that the ketobromide of tetrabromoparacresol is also considered, as well as the pentabromides from ortho- and meta-cresol, and from metaxylenol. The formation of a parahydroxyketone by the action of nitric acid on tetrachloroparacresol, &c., has been shown to be preceded by the formation of a paranitroketone, $NO_2{\cdot}CMe{<}^{CCl:CCl}_{CCl:CCl}{>}CO$.

C. F. B.

Reversible Transformation of Styrene and Metastyrene under the Influence of Heat. By GEORGES LEMOINE (*Compt. rend.*, 1897, **125**, 530—533).—The author has investigated the effect of

heat on styrene at 97°, 160°, 240°, 310° and 350° the styrene and metastyrene in the product being separated by distillation under low pressure at a temperature not exceeding 100°. The styrene used boiled at 142—144° under a pressure of 751 mm., at about 53—54° under a pressure of 1·8 mm. and 48·5 at 0·9 mm. Its sp. gr. was 0·920 at 0°, 0·910 at 12·1°, 0·908 at 16·5°, 0·899 at 27·1°, 0·879 at 51·5° and 0·852 at 87°.

Whether the original substance is styrene or metastyrene, the composition of the product tends towards the same limit under a given set of conditions; provided the temperature is the same throughout the whole of the apparatus, the quantity of styrene that remains unaltered depends on the volume of matter heated, or, in other words, the limit corresponds with a given vapour pressure, as in cases of dissociation. The rate of change is at first somewhat rapid but gradually becomes slower and slower. The limit as determined in flasks of somewhat considerable capacity is not quite the same as the limit determined in narrow glass tubes, the difference being most probably due to the disturbing influence of the walls.

At about 97°, the conversion of styrene into metastyrene is practically complete, but the proportion of styrene remaining increases slightly with the temperature and is 0·9 gram per litre at 310°, the corresponding vapour pressure being 0·4 atmos.

Details of the observations are given in the paper. C. H. B.

Nitroso-derivatives of Catechol Methyl Ether [Guaiacol]. By A. Pfob (*Monatsh.*, 1897, 18, 467—480).—Guaiacol (catechol methyl ether, $OH·C_6H_4·OMe = 1:2$) can be made to yield a nitroso-derivative by dissolving it in alcohol, adding acetic acid, cooling to $-2°$, adding potassium nitrite gradually, allowing to remain at this temperature, and finally diluting with ice and water. The product, 2-methoxy-1 : 4-quinone-4-monoxime, $O:C_6H_3(OMe):NOH$ or $OH·C_6H_3(OMe)·NO$, is identical with Best's paranitrosoguaiacol (Abstr., 1890, 608), and yields the same 2-methoxy-1 : 4-quinonedioxime when treated with hydroxylamine hydrochloride. When boiled with excess of acetic anhydride, it yields a *monacetyl* derivative, $O:C_6H_3(OMe):NOAc$, which melts and decomposes at 156—158°; when reduced with stannous chloride, it yields 4-*amido-2-methoxyphenol*, $OH·C_6H_3(OMe)·NH_2$, an unstable base the *hydrochloride* of which was prepared, as also the *triacetyl* derivative, $OAc·C_6H_3(OMe)·NAc_2$, which melts at 101°, and yields the hydrochloride of the methoxyamidophenol when it is treated with hydrochloric acid. When the monoxime is heated with water for several hours at 150—160°, a small quantity of 2-methoxy-1 : 4-quinol, $OH·C_6H_3(OMe)·OH$, is perhaps formed; when it is heated at 100° with potassium methoxide and methylic iodide in the presence of ether, it yields a *methyl ether*, $O:C_6H_3(OMe):NOMe$, which melts at 105—106°, and forms amidomethoxyphenol when reduced with stannous chloride.

From catechol ethyl ether, yellow 2-*ethoxy*-1 : 4-*quinone-4-monoxime* can be obtained; when heated, it decomposes without melting.

C. F. B.

Derivatives of Guaiacol. By HANS RUPE (*Ber.*, 1897, **30**, 2444—2449).—The author has prepared several derivatives of guaiacol containing nitrogen groups in the para-position relatively to the hydroxyl.

Para-nitrosoguaiacol is most conveniently prepared by heating guaiacol, methylic alcohol, sodium methoxide and ethylic nitrite in a closed tube for 12 hours at 100°. *Paranitroguaiacol*, $OH\cdot C_6H_3(NO_2)\cdot OMe$ [$NO_2 : OH : OMe = 4 : 1 : 2$], formed from the nitroso-compound on oxidation with alkaline potassium ferricyanide, crystallises from hot water in slender, yellow needles melting at 103—104°. *Dinitroguaiacol*, $OH\cdot C_6H_2(NO_2)_2$ [$OH : OMe : (NO_2)_2 = 1 : 2 : 4 : 6$], melts at 123—124° and is formed when nitric acid acts on nitrosoguaiacol. *Paramidoguaiacol*, $OH\cdot C_6H_3(NH_2)\cdot OMe$, can be prepared either by reducing the azo-compound produced by the combination of diazobenzene chloride with guaiacol by means of tin and hydrochloric acid, or by reducing nitrosoguaiacol with stannous chloride and hydrochloric acid; it crystallises in glistening prisms melting and decomposing at 176—177°; the *hydrochloride* separates from hydrochloric acid in large, pale green crystals. Paracyanoguaiacol, $OH\cdot C_6H_3(CN)\cdot OMe$, prepared from the diazo-compound, is identical with the substance obtained by Markus from vanillin.

J. F. T.

Sitosterol. By RICHARD BURIÁN (*Monatsh.*, 1897, **18**, 551—574).—The "germs" of wheat or rye (a refuse product of flour-mills) are extracted with ether, the extracted fat is hydrolysed with alcoholic potash, and the solution is precipitated with calcium chloride. The precipitate of calcium soap and other substances thus obtained is extracted with acetone, the extract is evaporated to dryness and dissolved in ether, the ethereal solution is washed cautiously with dilute hydrochloric acid and potassium hydroxide in succession, and is then evaporated to dryness; the residue is finally crystallised from methylic alcohol. In this way, a substance, $C_{27}H_{44}O + H_2O$, is obtained which resembles the cholesterol of bile in external appearance and in composition, but melts at 137·5°, and in ethereal solution has the specific rotation $[\alpha]_D = -26·71°$; it is named *sitosterol* (σῖτος = wheat, corn). It is an unsaturated substance, for it forms a *dibromide*, which does not crystallise easily, and is difficult to purify; it melts and decomposes at about 98°. It also forms a *monacetate*; this melts at 127° after softening at 124·5°, and yields a *dibromide* which also crystallises with difficulty; a *propionate* and *benzoate*, melting respectively at 108·5° and 145—145·5°, were also prepared. *Sitosterylic chloride*, $C_{27}H_{43}Cl$, can be obtained by the action of phosphorus pentachloride on sitosterol; it melts at 87·5° after softening at 82°, and is reduced by sodium in boiling amyl alcoholic solution to *sitostene*, $C_{27}H_{44}$, which melts between 61° and 68°, according to the rapidity with which it is heated, has in ethereal solution the specific rotation $[\alpha]_D = -38·79°$, and is an unsaturated hydrocarbon, forming a *dibromide* which crystallises with difficulty, and melts between 105—110° after softening at 70°.

The methyl alcoholic mother liquor from the sitosterol contains another substance, *parasitosterol*, which melted at 132·5°; after con-

version into the acetate and recovery from the latter by hydrolysis with sodium methoxide, at 127·5°; it resembles sitosterol in appearance. This substance appears also to have the composition $C_{27}H_{44}O$, but in ethereal solution it has the specific rotation $[\alpha]_D = -20·8°$, and its *monacetate* melts at 115—120°, and forms a *dibromide* which melts at 112° after softening at 104·5°.

Finally, a tabulated list is given of all the phytosterols (vegetable cholesterols) at present known, with their specific rotations, and the melting points and crystalline form of themselves and their acetates and benzoates. C. F. B.

Formation of Chains: XVII. Orthotoluidine and Metatoluidine; XVIII. Paratoluidine; XIX. Metaxylidine. By Carl A. Bischoff (*Ber.*, 1897, 30 2464—2468, 2469—2475, 2476—2480. Compare this vol., i, 10).—Aromatic amines, $R_I·NH_2$, were heated with ethylic salts of α-bromo-acids, $CR_{II}R_{III}Br·COOEt$. The products of the reaction are $R_I·NH·CR_{II}R_{III}·COOEt$ and $R_I·NH_3Br$; to determine the extent to which the reaction has taken place, the amine hydrobromide was washed with chloroform and weighed; the error was not greater than ±2 per cent. As a rule, the temperature employed was 120°, and the heating was continued for 4 hours; experiments were also made at 130—135° and at 180°, and the products of these were submitted to fractional distillation, the fractions being weighed and a fractionation curve constructed. Some experiments were also made at 100°. The numbers in Table I. give the extent, in percentages of the theoretical maximum, to which the reaction takes place between the amines and ethylic salts there tabulated; the amount of reaction between the amines and certain acids, $R_{II}·COOH$, was also determined, each pair of substances being heated together for 1 hour at 100°, the product being, of course, a substance of the type $R_{II}·CO·NHR_I$; Table II. gives the results.

TABLE I.

	Ethylic salt.	Aniline.	2-Toluidine.	3-Toluidine.	4-Toluidine.	1:3:4-Xylidine.
At 100°.	Bromopropionate	95	54	94	92	91
	Bromophenylacetate	68	43	47	43	68
	Bromisobutyrate	29	19	62	38	19
At 120°	Bromopropionate	94	97	94	93	96
	Bromobutyrate	86	84	87	92	89
	Bromisobutyrate	66	40	81	77	61
	Bromisovalerate	23	15	19	38	14

TABLE II.

R_{II} ($R_{II}·COOH$).	2-Toluidine.	4-Toluidine.	1:3:4-Xylidine.
H	92·2	95	94·6
CH_3	17·6	31·6	26·2
CH_2Me	7·2	11·9	3·6
$CH_2Et·CH_2$	4·2		1·8
CH_2Et	2·7	3·0	0·9
$CHMe_2$	1·4	3·4	0·3
$CHMe_2·CH_2$		0·0	
$OH·CH_2$	28·4	44·6	20·4
$OH·CHMe$	20·4	26·5	11·8
$OH·CHPh$	14·1	14·7	6·1
$OH·CHEt$	14·5		4·9
$OH·CMe_2$	0	1·2	2·4

The following new substances were prepared in the course of the investigation. *Ethylic a-orthotoluidoisovalerate*,

$$C_6H_4Me\cdot NH\cdot CH(CHMe_2)\cdot COOEt,$$

melts at 30° and boils at 282—284° under 763 mm. pressure; the corresponding *acid* melts at 101°, and loses carbonic anhydride when distilled, yielding *isobutylorthotoluidine*, which boils at 230—235° under 758 mm. pressure. *Ethylic metatoluidopropionate*,

$$C_6H_4Me\cdot NH\cdot CHMe\cdot COOEt,$$

boils at 271—276° under 767 mm. pressure; *ethylic metatoluidobutyrate*, $C_6H_4Me\cdot NH\cdot CHEt\cdot COOEt$, at 281—285° under 745 mm.; and *ethylic metatoluidoisobutyrate* at 270—273° under 753 mm., and at 205—210° under 104 mm. pressure; *ethylic α-metatoluidophenylacetate*, $C_6H_4Me\cdot NH\cdot CHPh\cdot COOEt$, melts at 109°. *Ethylic α-paratoluidoisovalerate* boils at 295° under 753 mm. pressure; the corresponding acid melts at 110°. *Ethylic α-paratoluidophenylacetate* melts at 85—86°. When paratoluidine is heated with chloracetamide, eventually to 150°, *paratolylimidodiacetimide*, $C_6H_4Me\cdot N:(CH_2\cdot CO)_2:NH$, melting at 195°, is produced; whilst in the presence of sodium acetate, paratoluidoacetamide is formed instead. Paratoluidine with α-bromopropionamide at 80° yields toluidopropionamide, and at 150—180°, *α-paratoluidopropionic paratoluidide*, $C_6H_4Me\cdot NH\cdot CHMe\cdot CO\cdot NH\cdot C_6H_4Me$, which melts at 158°. With α-bromobutyramide and α-bromisobutyramide at 120—130°, it yields respectively *α-paratoluidobutyric* and *α-paratoluidoisobutyric paratoluidides*, melting at 138° and 144°. *Ethylic α-metaxylidopropionate*, $C_6H_3Me_2\cdot NH\cdot CHMe\cdot COOEt$, melts at 42° and boils at 274—275° under 753 mm. pressure. *Ethylic α-metaxylidobutyrate*, $C_6H_3Me_2\cdot NH\cdot CHEt\cdot COOEt$, boils at 285—290° under 753 mm. *Ethylic metaxylidophenylacetate*, $C_6H_3Me_2\cdot NH\cdot CHPh\cdot COOEt$, melts at 90·5°.

C. F. B.

Nitrosoanilines. By M. C. Schuyten (*Chem. Zeit.*, 1897, **21**, 24). —By passing nitric oxide gas through an alcoholic solution of aniline, the author obtained nitraniline, but no nitroso-derivative.

E. W. W.

Paratolyltrimethylenediamine and γ-Iodopropylamine. By Martin Fränkel (*Ber.*, 1897, **30**, 2497—2510).—By heating γ-bromopropylphthalimide, $C_8H_4O_2:N\cdot[CH_2]_2\cdot CH_2Br$ (1 mol.), with paratoluidine (2 mols.), eventually at 150°, yellow *paratoluidopropylphthalimide*, $C_8H_4O_2:N\cdot[CH_2]_3\cdot NH\cdot C_7H_7$, melting at 134—136°, is obtained; the white *hydrochloride* melts at 198°, and is decomposed by water. If a relatively smaller amount of the toluidine is used, the product is yellow *paratoluidodipropyldiphthalimide*, $(C_8H_4O_2:N\cdot[CH_2]_3\cdot)_2N\cdot C_7H_7$, melting at 124°. When paratoluidopropylphthalimide is boiled with 20 per cent. hydrochloric acid, *paratolyltrimethylenediamine*, $NH_2\cdot[CH_2]_3\cdot NH\cdot C_7H_7$, is formed (Balbiano, Abstr., 1889, 1216); this boils at 283° under 763 mm. pressure, and has a sp. gr. = 1·0253 at 15°; the hydrochloride, with 2HCl, melts at 257°, the yellow *platinochloride* at 205°, and the greenish-yellow *picrate* at 113°; the base absorbs carbonic anhydride from the air. With potassium cyanate and hydrochloric acid, it forms *paratoluidopropylcarbamide*,

$$NH_2\cdot CO\cdot NH\cdot[CH_2]_3\cdot NH\cdot C_7H_7,$$

which melts at 152° losing ammonia; after prolonged heating at 212°, the residue is found to be *paratolyltrimethylenecarbamide*,

$$CO<\begin{matrix}N(C_7H_7)\cdot CH_2\\NH\text{——}CH_2\end{matrix}>CH_2,$$

melting at 207°. With potassium thiocyanate and hydrochloric acid at 140°, it yields *paratolyltrimethylenethiocarbamide*,

$$CS<\begin{matrix}N(C_7H_7)\cdot CH_2\\NH\text{——}CH_2\end{matrix}>CH_2,$$

melting at 188°. With carbon bisulphide, it forms the *dithiocarbamate*, $NH(C_7H_7)\cdot[CH_2]_3\cdot NH\cdot CS\cdot SNH_3\cdot[CH_2]_3\cdot NH\cdot C_7H_7$, which melts at 125°, and decomposes at that temperature, or when boiled with water, into hydrogen sulphide, paratolyltrimethylenediamine, and paratolyltrimethylenethiocarbamide. With nitrous acid, it yields *amidopropylparatolylnitrosamine*, $NH_2\cdot[CH_2]_3\cdot N(C_7H_7)\cdot NO$, the *hydrochloride* of which melts at 175°; the nitrosamine itself is an oil which decomposes when distilled, and absorbs carbonic anhydride from the air. When paratoluidopropylphthalimide is heated with methylic iodide at 125°, the product is *γ-iodopropylphthalimide*, $C_6H_4O_2{:}N\cdot[CH_2]_3\cdot I$, melting at 88°, and methylparatoluidine.

By heating γ-bromopropylphthalimide with methylparatoluidine at 170°, yellow *methylparatoluidopropylphthalimide*,

$$C_8H_4O_2{:}N\cdot[CH_2]_3\cdot NMe\cdot C_7H_7,$$

melting at 125°, is obtained.

γ-Iodopropylphthalimide (see above) is more conveniently obtained by boiling γ-bromopropylphthalimide with aqueous alcoholic sodium bromide. When boiled with hydriodic acid of boiling point 127°, it yields *γ-iodopropylamine*, $NH_2\cdot[CH_2]_2\cdot CH_2I$, isomeric with a compound previously prepared by Hofmann and by Gabriel (Abstr., 1897, i, 136). This is an unstable oil; the *hydriodide* melts at 166°, the yellow *picrate* at 134—135°; its benzoyl derivative, *γ-iodopropylbenzamide*,

$$NHBz\cdot[CH_2]_2\cdot CH_2I,$$

melts at 68°, and reacts with paratoluidine at 170°, forming crystalline *benzoparatolyltrimethylenediamide*, $NHBz\cdot[CH_2]_3\cdot NH\cdot C_7H_7$. With paratolylthiocarbimide, $CS{:}NC_7H_7$, in ethereal solution, γ-iodopropylamine yields a substance which is probably *paratolyltrimethylene-ψ-thiocarbamide*, $CH_2<\begin{matrix}CH_2\cdot N\\CH_2\cdot S\end{matrix}>C\cdot NH\cdot C_7H_7$; this melts at 135°, the hydriodide at 200°, the reddish-yellow *platinochloride* at 208°, and the yellow *picrate* at 170°. C. F. B.

Action of Diazomethane on Nitrosobenzene. By Hans von Pechmann (*Ber.*, 1897, **30**, 2461—2463).—The action of diazomethane on nitrosobenzene in ethereal solution leads to the formation of a yellow, crystalline substance melting at 182—183°, which is apparently *glyoxime-N-phenylether*, $\begin{matrix}O\text{—}\\|\\NPh\end{matrix}>C_2H_2<\begin{matrix}O\\|\\NPh\end{matrix}$; the yield is about 50 per cent. of the theoretical, and phenylhydroxylamine is formed as a bye-product, which makes it probable that part of the nitrosobenzene has acted as an oxidising agent. This new substance has been prepared by Bamberger from formaldehyde and phenylhydroxylamine (*Vierteljahrschr.*

d. naturforsch. Ges. in Zürich, 1896, 178); acids decompose it into glyoxaldehyde and phenylhydroxylamine, from which two substances it can be prepared synthetically; heating with acetic anhydride converts it into oxanilide, or derivatives of this. C. F. B.

Diazocyanides and Double Salts of Diazonium Cyanides. By ARTHUR R. HANTZSCH and KARL DANZIGER (*Ber.*, 1897, **30**, 2529—2548. Compare Abstr., 1895, i, 348).—The diazonium cyanides cannot be obtained in the pure state, but their double salts are formed when a solution of a diazonium chloride is treated with silver cyanide or a neutralised solution of potassium cyanide. The presence of hydroxyl ions, which are invariably present in ordinary potassium cyanide solution, causes the formation of the insoluble *syn*-diazocyanide. The double salts with silver cyanide are colourless, soluble in water, and of neutral reaction, and are at once decomposed by acetic acid, whilst in aqueous solution they gradually decompose, forming nitrogen, hydrogen cyanide, silver cyanide, and a phenol. They thus closely resemble the double cyanide of silver and potassium. This behaviour also renders it probable that the free diazonium cyanide itself would resemble potassium cyanide, and therefore differ essentially from the normal diazocyanide, which is stable towards acids.

ψ-Cumenediazonium silver cyanide, $C_6H_2Me_3\cdot\underset{N}{\overset{}{N}}\!\!\vdots\cdot CN,AgCN$, has only been obtained in aqueous solution and is prepared from the diazonium iodide and silver cyanide. It readily forms azo-colouring matters. *Parabromodiazonium silver cyanide*, $C_6H_4Br\cdot\underset{N}{\overset{}{N}}\!\!\vdots\cdot CN,AgCN$, has been obtained in small quantity in the form of a crystalline powder, which explodes at 119—120°.

Of the stereoisomeric diazocyanides, $R\cdot N{=}N\cdot CN$, the syn- or normal compounds, $\begin{array}{l}R\cdot N\\ \quad\ \| \\ CN\cdot N\end{array}$, are the primary products of reaction, are labile, have a low melting point, readily form azo-colouring matters, and can be directly decomposed into nitrogen and a nitrile. The anti- or isodiazocyanides, on the other hand, are stable, have a high melting point, and do not easily form azo-colouring matters or decompose into nitrogen and a nitrile. As will be seen from the description of the various compounds, the presence of negative groups increases the stability of the syn-form, a group having a greater effect in the ortho- than in the para-position; the presence of halogens also diminishes the readiness with which both series undergo reaction. Diorthocyanides are decomposed into nitrogen and a dihalogen derivative of benzene by alcohol and an alkali, whereas all other halogen diazocyanides are thus converted into diazoimido-ethers.

Alcohol radicles appear to be unfavourable to the formation of stable cyanides of either series.

Syn-*parabromobenzenediazocyanide*, $\begin{array}{l}C_6H_4Br\cdot N\\ \qquad\quad\ \| \\ \qquad CN\cdot N\end{array}$, is obtained by adding aqueous potassium cyanide to parabromobenzenediazonium chloride solution at −10°; it forms yellow needles melting at 42°, reacts

violently with precipitated copper, and forms bromobenzeneazonaphthol with β-naphthol. If kept for a day, or dissolved in alcohol and precipitated by water, at the ordinary temperature, it passes into the *anti*-cyanide, $\begin{matrix} Br\cdot C_6H_4\cdot N \\ \quad\quad\quad \| \\ \quad\quad\quad N\cdot CN \end{matrix}$, which crystallises from light petroleum in brown needles melting at 129—130°; this is indifferent towards β-naphthol and copper powder. Syn-*paraiodobenzenediazocyanide* is yellowish-brown and melts at 48°; the *anti*-cyanide crystallises in reddish-brown needles and melts at 152°. Syn-*orthobromobenzenediazocyanide* forms yellow needles and melts at 51°; it does not pass into the isomeride at the ordinary temperature, but when precipitated by water from alcoholic solution at the ordinary temperature, a small quantity of the *anti*-compound is formed, which melts at 107—108°. Syn-*metabromobenzenediazocyanide* forms very unstable needles melting at 25—26°. The *anti*-salt has not yet been obtained.

Syn-2 : 4-*dibromobenzenediazocyanide* melts at 70—71°, is stable, and only passes into the *anti*-salt at the summer temperature; the latter crystallises from dilute alcohol in reddish-brown plates melting at 141°. Both forms are converted by alcohol and hydrogen chloride into 2 : 4-*dibromodiazocarbamide*, $C_6H_3Br_2\cdot N_2\cdot CO\cdot NH_2$, which crystallises in orange-coloured needles melting at 194°. Alcoholic potash converts it into *potassium dibromodiazocarboxylate*, which forms golden-yellow plates and yields a yellow precipitate of the *free acid* on acidification. The syn-*dichlorocyanide* changes more readily than the dibromo-compound into the *anti*-compound. Syn-2 : 4-*di-iodobenzenediazocyanide* melts at 96°, the *anti*-cyanide at 186°. Syn-3 : 4-*dibromobenzenediazocyanide* melts at 56—57°; it changes in a few days into the *anti*-cyanide, which crystallises from light petroleum in small, brown needles melting at 100—101°. Syn-2 : 5-*dibromobenzenediazocyanide* melts at 42—43°, and in a few days changes into the *anti*-cyanide, which crystallises from dilute alcohol in brick-red needles melting at 122—123°. Syn-3 : 5-*dibromobenzenediazocyanide* melts at 60°, and decomposes if kept; the *anti*-compound melts at 85°. Syn-2 : 6-*dibromobenzenediazocyanide* melts at 44—45°, and decomposes completely when kept, or if it is precipitated from alcoholic solution at the ordinary temperature. The *anti*-compound has not been obtained.

Syn-2 : 4 : 6-*tribromobenzenediazocyanide*, which forms yellow plates melting at 59—60°, is remarkably stable, does not change when kept, and only reacts slowly with β-naphthol and with copper; with alcohol and soda, it yields tribromobenzene and nitrogen. The *anti*-salt can only be obtained with difficulty and forms brownish-red crystals melting at 147°; alcohol and caustic soda convert it into the corresponding diazoimidoether. Syn-*symmetrical*-2 : 4 : 6-*trichlorobenzenediazocyanide* is much less stable than the tribromo-compound; the *anti*-compound has not been obtained. Syn-2 : 4 : 5-*trichlorobenzenediazocyanide* melts at 55° and is very stable; the *anti*-cyanide crystallises in red needles melting at 100—101°. Alkyl-diazocyanides can only be prepared by adding the diazonium salt to an excess of potassium cyanide solution at −12°. The *toluene*-derivative is oily, the *asymmetrical metaxylenediazocyanide* is solid, but rapidly decomposes.

Syn-*ψ-cumenediazocyanide* forms dark red crystals melting at 38—39°; the *anti*-compound has not been prepared. Syn-*bromometaxylenediazocyanide* melts at 49—50° and readily passes into the *anti*-compound which melts at 64—65°. Syn-*paramethoxybenzenediazocyanide* melts at 50°, and changes in a few days into the *anti*-cyanide melting at 122°.

Syn-*α-naphthalenediazocyanide* melts at 57—58° and changes completely and readily into the *anti*-cyanide, which crystallises in reddish-brown needles and melts at 116°.

Syn-*β-naphthalenediazocyanide* melts at 51—52° and rapidly passes into the *anti*-compound, which crystallises from hot alcohol in yellowish red needles melting at 131°. A. H.

Additive Products of Azo- and Diazo-compounds with Benzenesulphinic Acid. By ARTHUR R. HANTZSCH and R. GLOGAUER (*Ber.*, 1897, **30**, 2548—2559. Compare Abstr., 1897, i, 222).—Azo-compounds and both normal and iso-diazo-compounds unite with benzenesulphinic acid to form colourless compounds when an alcoholic solution of the azo- or diazo-compound is added to a similar solution of benzenesulphinic acid. These are stable towards acids, but are decomposed by alkalis, are probably derivatives of hydrazobenzene, and are formed by direct addition. When the solutions are mixed in the inverse order, phenylsulphones are formed as a rule. Diazonium compounds, on the other hand, only react with benzenesulphinic acid to form diazosulphones, so that this reaction affords a purely chemical proof of the constitution of the normal diazocyanides, which combine with benzenesulphinic acid, and therefore cannot have the diazonium formula. Both *syn*- and *anti*-diazo-compounds yield the same additive product, the asymmetry of the azo-group disappearing when a derivative of ammonia is produced. On decomposition with alkalis, the additive product formed from either diazocyanide yields benzenesulphinic acid and the *anti*-diazocyanide, so that the *syn*-cyanide can in this way be converted into its isomeride.

Phenylsulphonehydrazobenzene (benzenesulphinic acid azobenzene), $NHPh\cdot NPh\cdot SO_2Ph$, is obtained by adding an alcoholic solution of azobenzene to a similar solution of benzenesulphinic acid; it crystallises in pure white, silky needles melting at 107°. *Phenylsulphonehydrazochlorobenzene cyanide*, $PhSO_2\cdot N(C_6H_4Cl)\cdot NH\cdot CN$, is prepared from parachlorobenzenediazocyanide and decomposes at 131°; the corresponding *bromo*-derivative decomposes at 127°.

Syn-2 : 6-dibromobenzenediazocyanide, which is itself very unstable, yields a remarkably stable *hydrazo*-compound with benzenesulphinic acid which melts at 168°; aqueous potash converts it into a coloured stable substance which also melts at 168°, and is probably the *anti*-cyanide. *Syn*-tribromobenzenediazocyanide readily unites with benzenesulphinic acid, in whatever order the solutions are mixed, to form a colourless compound, which decomposes at 162°; treatment with aqueous potash produces the *anti*-cyanide, which is best prepared in this way.

Parabromobenzenediazocarbamide-benzenesulphinic acid,

$$PhSO_2\cdot N(C_6H_4Br)\cdot NH\cdot CO\cdot NH_2,$$

is formed by the combination of its constituents and melts at 151°; the

additive compound formed from chlorobenzenediazoimido-ether melts at 138°.

Benzenediazophenylsulphone and bromobenzenediazoimidocyanide also form similar compounds, the derivative of the latter decomposing at 118°. The two stereoisomeric nitrobenzenediazocyanides do not appear to behave in this way; phenylenediazosulphide does not unite with benzenesulphinic acid, whilst ethylic diazoacetate is decomposed by it even at low temperatures. The compound formed from orthodiazobenzoic acid and benzenesulphinic acid, which was previously described by Hantzsch and Singer, probably possesses the hydrazo-constitution, $C_6H_4<\begin{matrix}CO——O\\N(SO_2Ph)\cdot NH\end{matrix}$ or $C_6H_4<\begin{matrix}CO\cdot O\\NH\cdot N\cdot SO_2Ph\end{matrix}$. *Orthodiazobenzoparatoluenesulphinic acid*, $C_6H_4<\begin{matrix}CO——O\\N(SO_2C_7H_7)\cdot NH\end{matrix}$, melts and decomposes at 160°, and is at once decomposed by caustic alkalis into toluenesulphinic acid and salicylic acid.

Orthodiazobenzoparabromobenzenesulphinic acid melts at 181°, and yields a very unstable, yellow salt with concentrated aqueous soda.

A. H.

Tetrazotic, Oxytetrazotic, and Dioxytetrazotic Acids. By WILHELM C. LOSSEN (*Annalen*, 1897, **297**, 322—325. Compare Abstr., 1892, 51).—Ferric chloride is a useful agent for recognising many dioxytetrazotic acids, as, for example, benzenyldioxytetrazotic acid and paratolenyldioxytetrazotic acid, with which it develops a red coloration, and forms an iron derivative which dissolves in ether.

Benzenyldioxytetrazotic acid and many of its salts are decomposed in accordance with the equation $C_6H_5\cdot CN_4O_2H = C_6H_5\cdot CN + N_2 + HNO_2$ under the influence of feeble bases. In the case of dioxytetrazotic acid, this decomposition is spontaneous, nitrous acid being set free, moreover, potassium benzenyldioxytetrazotate liberates nitrogen and yields potassium benzoate when the solution is boiled; the occurrence of one or other of these changes depends, not only on the circumstances of the experiment, but also on the nature of the acid.

It is noteworthy that benzenyldioxytetrazotic and paratolenyldioxytetrazotic acids are readily converted into the amidines from whence they are derived; treatment of the former substance with hydrochloric acid followed by ammonia gives rise to the benzenylamidine salt of benzenyldioxytetrazotic acid.

In spite of the fact that all attempts to couple the dioxytetrazotic acids with phenols have proved unsuccessful, the formula

$$NO\cdot N\colon C(C_xH_y)\cdot N\colon NOH,$$

most nearly expresses their chemical behaviour, although it must be admitted that they differ from other diazo-compounds in forming additive compounds, instead of diazoamido-derivatives, with amines.

M. O. F.

Benzenyldioxytetrazotic Acid. By WILHELM C. LOSSEN and MAX GRONEBERG (*Annalen*, 1897, **297**, 325—349. Compare Lossen and Mierau, Abstr., 1891, 1038).—The benzenylamidine salt of benzenyldioxytetrazotic acid crystallises from alcohol in regular quadratic leaflets, and from water in yellowish, prismatic crystals; it

explodes at 178°, or at 171° when heated slowly. The potassium salt is also yellowish, and when the aqueous solution is boiled, yields nitrogen and potassium benzoate in quantitative amount. The *ammonium* salt, obtained by adding ammonium chloride to a solution of the potassium salt, crystallises in long, colourless prisms; it dissolves readily in water and alcohol, explodes at 137°, and when heated with water yields nitrogen and ammonium benzoate. The *hydrazine* salt forms microscopic, six-sided plates, scarcely soluble in cold water or alcohol, and insoluble in ether; it explodes at 60°, and also when rubbed in a mortar. When an alcoholic solution of the hydrazine salt is heated on the water-bath, nitrogen is liberated at 35°, two-fifths of the theoretical amount being obtained; benzonitrile is also produced, along with ammonium benzenyltetrazotate, whilst, on one occasion, benzenylamidine benzenyldioxytetrazotate was formed. The *aniline* salt of benzenyldioxytetrazotate is obtained as a yellowish-white powder which is insoluble in ether, and dissolves with difficulty in water; it crystallises from alcohol in white needles, and explodes at 93°. When the salt is treated with boiling water, nitrogen, benzonitrile, and phenol are produced, along with an amorphous *compound* having the formula $C_{22}H_{17}N_3O$. The *paratoluidine* salt also crystallises from alcohol in colourless needles, decomposes at 105°, and when boiled with water yields benzonitrile, paracresol, and nitrogen.

No definite product is obtained by the action of dimethylaniline on dioxytetrazotic acid. When a solution of the base in normal sulphuric acid is added to an aqueous solution of the potassium salt, and the liquid boiled, an intense green coloration is developed, and gas is evolved, whilst a brown, tarry substance separates; this *compound* is precipitated from chloroform by light petroleum, and has the composition $C_{24}H_{32}N_4O$.

The *phenylhydrazine* salt of benzenyldioxytetrazotic acid is very sparingly soluble in water, and crystallises from alcohol in needles which explode at 90°; when heated with water, it yields benzonitrile, and the same change occurs spontaneously.

The behaviour of benzenyldioxytetrazotic acid towards ferric chloride is very characteristic. On treating the potassium salt with neutral ferric chloride, a dark, violet-brown precipitate is at once formed, and yields a dark, reddish-brown solution on agitation with ether; the ethereal solution, however, is very unstable, and if separated from the aqueous liquid, gradually deposits a reddish-brown powder, and becomes colourless, yielding benzoic acid on evaporation. If the original precipitate is filtered before agitation with ether, it explodes feebly when heated in the dry state; treatment with caustic potash gives rise to potassium dioxytetrazotate.

Experimental details relating to the decomposition of benzenyldioxytetrazotic acid by acids, and the regeneration of benzenylamidine (compare foregoing abstract) are described in the paper. M. O. F.

Paratolenyldioxytetrazotic Acid. By Wilhelm C. Lossen, Franz Hess, Carl Kirschnick, and Paul Schneider (*Annalen*, 1897, **297**, 349—353. Compare foregoing abstracts).—The *paratolenyl-*

amidine salt of paratolenyldioxytetrazotic acid, $C_8H_8N_4O_2,C_8H_{10}N_2$, is obtained by adding a concentrated solution of potassium nitrite (38 grams) to a concentrated solution of paratolenylamidine hydrochloride (20 grams), dissolving the crystalline precipitate in cold water, and treating the solution with 63 per cent. nitric acid (11 grams). It crystallises from boiling water in yellowish, rhombic leaflets, and yields rectangular prisms when recrystallised from alcohol; in the latter form, it explodes at 195—198°. The *potassium* salt separates from concentrated, aqueous solutions in colourless leaflets containing $1H_2O$, which is removed in the desiccator; even in the moist condition, the salt is highly explosive, and the aqueous solution yields nitrogen and paratoluic acid when boiled or submitted to the influence of sunlight. The *ammonium* salt crystallises in colourless needles, and explodes at 130°; the alcoholic and aqueous solutions, when boiled, liberate nitrogen, and yield ammonium toluate on evaporation. The *pyridine* salt is crystalline, and explodes when heated; it dissolves in water and alcohol, but is insoluble in ether. The *hydroxylamine*, *aniline*, *barium*, and *silver* salts are explosive solids. Ferric chloride has the same action on the potassium salt as on the potassium salt of benzenyldioxytetrazotic acid, yielding a highly unstable precipitate which forms a brownish-red solution in ether. M. O. F.

Decomposition of Potassium Paratolenyldioxytetrazotate by Hydrochloric Acid. By WILHELM C. LOSSEN and FRANZ HESS (*Annalen*, 1897, **297**, 354—370. Compare foregoing abstracts).—The action of mineral acids on salts of paratolenyldioxytetrazotic acid proceeds in the same direction as in the case of benzenyldioxytetrazotic acid, the chief product being paratoluonitrile. If, however, a cold, saturated solution of potassium paratolenyldioxytetrazotate is treated with 1 mol. proportion of a normal solution of hydrochloric acid, and agitated during five minutes, a dark green substance is precipitated, which, if allowed to remain in the liquid, gradually becomes converted into toluonitrile, yielding nitrogen. The greenish-yellow *compound* (*Säurefällung*) must be collected, washed with alcohol and ether, rapidly dried in a current of air, and preserved in thin, interrupted layers, protected from the light; even then the substance becomes colourless spontaneously, but if these precautions are not observed, a violent explosion takes place. It is evident that this substance does not consist of free paratolenyldioxytetrazotic acid, as the precipitation is slow, although the product is insoluble in water; moreover, it is found that the filtrate contains in the unaltered state upwards of one-half the dioxytetrazotic acid employed.

The unstable compound obtained by the action of hydrochloric acid on potassium paratolenyldioxytetrazotate becomes yellowish-white when treated with chloroform, which is caused to boil by the vigour of the action; nitric oxide is evolved in this change, but if the chloroform is artificially cooled, nitrogen is the sole gaseous product. The insoluble residue consists of paratolenylamidine paratolenyldioxytetrazotate, the filtrate containing paratoluonitrile with 10 per cent. of paratoluic acid.

The same products arise when the compound undergoes spontaneous decomposition. Under the influence of ammonia, added to the liquid in which the compound has been precipitated, it yields paratolenylamidine

paratolenyldioxytetrazotate, but if the substance is first isolated, and then treated with dilute ammonia until the alkaline action persists, ammonium paratolenyldioxytetrazotate passes into solution, and a red compound remains undissolved. *Rubamidide*, $C_8H_9N_3O$, is the name given by the authors to this substance, which has the empirical formula of paratolenylamidine paratolenyldioxytetrazotate; it is also produced by the action of aniline, and the filtrate, on evaporation, yields paratoluic acid and ammonium paratolenyldioxytetrazotate. Rubamidide explodes somewhat violently at 60—65°, and is slowly decomposed by cold water; the solution in alcohol is red but rapidly becomes colourless, yielding paratoluonitrile. It is insoluble in ether, but yields gas when kept in contact with it, forming paratolenylamidine; alcoholic potash also liberates gas, and gives rise to toluonitrile and a small proportion of potassium dioxytetrazotate. The action of hot water converts rubamidide into toluonitrile and a small proportion of amidine paratolenyldioxytetrazotate, nitrogen being set free.

From these facts, it is clear that paratolenylamidine paratolenyldioxytetrazotate and rubamidide are distinct substances, although having the same empirical formula, which is also that of a nitrosoparatolenylamidine; it is quite possible, therefore, that rubamidide is a compound of the latter class. M. O. F.

Phenylglycolenyldioxytetrazotic Acid and Phenylglyoxenyldioxytetrazotic Acid. By WILHELM C. LOSSEN and FRANZ BOGDAHN (*Annalen*, 1897, **297**, 371—380. Compare foregoing abstracts).—*Phenylglycolenylamidine* (phenylhydroxyacetamidine) has been prepared by C. Beyer (Abstr., 1885, 983); the *nitrate* forms rhombic or monoclinic crystals, and melts and decomposes at 154°.

Phenylglycolenylamidine phenylglycolenyldioxytetrazotate,

$$C_8H_8N_4O_3,C_8H_{10}N_2O,$$

is obtained by adding potassium nitrite solution and a small quantity of nitric acid to a warm, aqueous solution of phenylglycolenylamidine hydrochloride (1 mol.), the product being treated alternately with potassium nitrite and nitric acid until a molecular proportion of each has been added. It is a crystalline powder which explodes when heated; it dissolves in alcohol, but is insoluble in alcohol and ether. The *potassium* salt crystallises from water, but decomposes on boiling the solution; it is highly explosive, and detonates when heated, or rubbed, or treated with concentrated sulphuric acid. The *barium* salt crystallises in aggregates; it is less explosive than the potassium salt. The *silver* salt is amorphous and colourless; it is an explosive substance, and rapidly darkens when exposed to light. The *aniline* salt crystallises in white leaflets, but rapidly becomes brown, and acquires the odour of aniline; it explodes when heated on platinum foil.

When an aqueous solution of potassium phenylglycolenyldioxytetrazotate is boiled, nitrogen is set free, and potassium mandelate produced; hot dilute sulphuric acid liberates a mixture of nitrogen and nitric oxide, and gives rise to mandelonitrile.

The *potassium* salt of phenylglyoxenyldioxytetrazotic acid,

$$COPh\cdot CN_4O_2K,$$

is obtained by oxidising potassium phenylglycolenyldioxytetrazotate

with potassium permanganate at 60°; it crystallises in long, lustrous, white needles, which become greenish-yellow in the desiccator, and forms a greenish-yellow solution in water. The salt explodes when heated, and also on treatment with concentrated sulphuric acid; a very dilute solution (1 : 7000) has a sweet, astringent taste.

The *silver* salt is a yellowish-brown, amorphous compound which is highly explosive.

The potassium salt of phenylglyoxenyldioxytetrazotic acid undergoes a characteristic change when the aqueous solution is boiled, yielding nitric oxide, nitrogen, benzoic acid, and hydrogen cyanide; the two last named are probably due to the intermediate production of the nitrile of benzoylformic acid. M. O. F.

β-Naphthenyldioxytetrazotic Acid. By WILHELM C. LOSSEN and GUSTAV GRABOWSKI (*Annalen*, 1897, **297**, 380—385. Compare foregoing abstracts).—*β-Naphthenylamidine β-naphthenyldioxytetrazotate*, $C_{11}H_8N_4O_2,C_{11}H_{10}N_2$, is prepared by adding potassium nitrite (2 mols.) to aqueous β-naphthenylamidine hydrochloride (1 mol.), dissolving in water the precipitate so formed, and treating the solution with concentrated nitric acid (1 mol.); it explodes at 180°, and gives Liebermann's reaction for nitroso-compounds. The *potassium* salt crystallises from water in yellowish needles, and explodes with exceptional violence when heated, or on treatment with concentrated sulphuric acid. The *silver* salt is also explosive.

β-Naphthenylamidine, employed in the production of the foregoing salts, has been prepared by Lohmann (*Ber.*, 1878, **11**, 1486), and melts at 145°; the *nitrite* crystallises from alcohol in colourless needles and melts at 122°. The *nitrate* is also crystalline, and the *platinochloride* forms slender, yellowish needles and melts at 216—217°.

It is noteworthy that anisenylamidine does not give rise to a dioxytetrazotic acid. M. O. F.

Tetrazotic, Oxytetrazotic, and Dioxytetrazotic Acids. By WILHELM C. LOSSEN (*Annalen*, 1897, **298**, 54—55).—A summary of the results described in the following abstracts. M. O. F.

Benzenyloxytetrazotic Acid. By WILHELM C. LOSSEN and FRIEDRICH FUCHS (*Annalen*, 1897, **298**, 55—67. Compare Lossen, Abstr., 1891, 1041).—Benzenyloxytetrazotic acid separates from a mixture of ether with a small quantity of alcohol in rhombic, hemihedral crystals; $a:b:c = 0·9506:1:0·6236$. Concentrated hydrochloric acid at 160° resolves the substance into benzonitrile, benzoic acid, and ammonium chloride, whilst concentrated sulphuric acid at 185° gives rise to metasulphobenzoic acid; nitric acid (sp. gr. = 1·53) acts vigorously on the compound, producing nitrobenzoic acid.

The *calcium* salt of benzenyloxytetrazotic acid crystallises from water in cubes, containing $3H_2O$, and the *sodium* salt contains $1H_2O$; the *cobalt* salt forms large, reddish crystals containing $2H_2O$, and the *copper* salt, which contains $3H_2O$, crystallises in green, microscopic needles. The *methylic* salt is crystalline, and melts at 40°; the *ethylic* salt is a yellowish oil, and yields benzoic acid, benzonitrile, ethylic chloride,

and ammonium chloride when heated in a sealed tube with concentrated hydrochloric acid at 160°. The *nitromethylic* salt, obtained by dissolving the methylic salt in nitric acid (sp. gr. = 1·53), crystallises from alcohol in long needles melting at 118°; reduction with stannous chloride and hydrochloric acid converts this substance into the *amidomethylic* salt, which crystallises from hot water in slender needles, and melts at 110°; the *hydrochloride* forms yellow plates.

M. O. F.

Paratolenyloxytetrazotic Acid. By WILHELM C. LOSSEN and PAUL SCHNEIDER (*Annalen*, 1897, **298**, 67—78).—*Paratolenyloxytetrazotic acid*, $C_8H_8N_4O$, obtained by reducing paratolenyldioxytetrazotic acid with 10 per cent. sodium amalgam, crystallises from water in slender, colourless needles, and from a mixture of ether and alcohol in lustrous prisms; it contains $1H_2O$, which is removed at 120°, and melts and decomposes at 172°, yielding paratoluonitrile, nitrogen, and nitrous oxide. Concentrated hydrochloric acid at 155° resolves the compound into paratoluic and paratolenyloxytetrazotic acids, the same effect being produced by concentrated sulphuric acid at 170°; nitric acid (sp. gr. = 1·105) gives rise to toluonitrile and paratoluic acid, the latter being also produced when paratolenyloxytetrazotic acid is heated with alcoholic ammonia at 160°. The *acid*, $C_8H_9N_3O$, a bye-product in the preparation of paratolenyloxytetrazotic acid, melts at 154°; the *calcium* salt contains $3H_2O$, and the *silver* salt is somewhat soluble in ether, alcohol, and hot water.

The *potassium* salt of paratolenyloxytetrazotic acid is anhydrous, and the *sodium* salt, which crystallises from alcohol in slender needles, contains $1\frac{1}{2}H_2O$; the *barium* and *calcium* salts contain $3H_2O$, the *cobalt* salt, which separates from water in small, red crystals, $2H_2O$, whilst the *copper* and *silver* salts are anhydrous. The *ethylic* salt is a colourless liquid, yielding paratoluonitrile, paratoluic acid, and ammonium chloride when heated with hydrochloric acid at 170°; the *methylic* salt is crystalline and melts at 44°.

M. O. F.

Phenethenyloxytetrazotic Acid. By WILHELM C. LOSSEN and ERNST KAMMER (*Annalen*, 1897, **298**, 78—88).—*Phenethenyloxytetrazotic acid*, $C_8H_8N_4O$, prepared by reducing phenethenyldioxytetrazotic acid with 10 per cent. sodium amalgam, crystallises from water in concentric groups of colourless needles; it melts at 135°, and explodes at higher temperatures. Caustic potash at 250° converts the substance into phenylacetic acid, but concentrated hydrochloric acid at 155° leaves the substance for the most part unchanged, a small quantity of nitrile and ammonium chloride being produced; concentrated sulphuric acid at 180° gives rise to sulphophenylacetic acid.

The *silver* salt of phenethenyloxytetrazotic acid is a white, amorphous powder, and melts at about 73°; the *copper* salt contains $3H_2O$. The *ammonium* salt crystallises in small, colourless needles, and melts at 145°, the *aniline* salt separates from ether in plates, and melts at 142°, and the *phenylhydrazine* salt melts at 157·5°. The *methylic* salt, which is a highly explosive, yellow liquid, yields a *nitro*-derivative when treated with nitric acid (sp. gr. = 1·53).

M. O. F.

Phenylglycolenyloxytetrazotic Acid. By WILHELM C. LOSSEN and FRANZ BOGDAHN (*Annalen*, 1897, **298**, 88—91).—*Phenylglycolenyloxytetrazotic acid*, $C_8H_8N_4O_2$, obtained by reducing phenylglycolenyldioxytetrazotic acid with 2 per cent. sodium amalgam, separates in small crystals on adding light petroleum to the alcoholic solution, and melts at 141°. The *silver* salt is white, and resists the action of light; the *barium* salt crystallises in thin leaflets, and is anhydrous.

M. O. F.

Benzenyltetrazotic Acid. By WILHELM C. LOSSEN and FRANZ STATIUS (*Annalen*, 1897, **298**, 91—105. Compare Lossen, Abstr., 1891, 1041).—Benzenyltetrazotic acid is most conveniently prepared by Pinner's method (Abstr., 1894, i, 386). The *sodium* salt crystallises in lustrous, highly refractive leaflets containing $3H_2O$, and the *calcium* salt, which forms transparent prisms, contains $4H_2O$; the *copper* salt is anhydrous, and the *ammonium* salt, which crystallises in white leaflets, undergoes dissociation when heated. The *methylic* salt separates from a mixture of alcohol and ether in transparent, prismatic crystals, and melts at 40°. When benzenyltetrazotic acid is heated alone at 218°, nitrogen is evolved, and a mixture of diphenyltriazole and diphenyltetrazine produced.

Bromobenzenyltetrazotic acid, $C_7H_5N_4Br$, is obtained by heating benzenyltetrazotic acid with bromine and water at 160° during 16 hours; it crystallises from dilute alcohol in flat, transparent prisms, and melts at 265°. *Nitrobenzenyltetrazotic acid*, $NO_2 \cdot C_7H_5N_4$, is formed when benzenyltetrazotic acid is dissolved in nitric acid (sp. gr. = 1·55) mixed with concentrated sulphuric acid; it cystallises from water, and melts at 145°. The *barium* salt contains $3H_2O$, and the *silver* salt, which is yellowish-white, resists the action of light.

M. O. F.

Paratolenyltetrazotic Acid. By WILHELM C. LOSSEN and CARL KIRSCHNICK (*Annalen*, 1897, **298**, 105—107).—Paratolenyltetrazotic acid, $C_8H_8N_4$, obtained by reducing paratolenyldioxytetrazotic acid with sodium amalgam, crystallises from alcohol in small needles, and melts at 248°. (Compare Pinner and Caro, Abstr., 1895, i, 137.)

M. O. F

Anisenyltetrazotic Acid. By WILHELM C. LOSSEN and JAMES COLMAN (*Annalen*, 1897, **298**, 107—116).—*Anisenyltetrazotic acid*, $OMe \cdot C_6H_4 \cdot CN_4H$, which is best prepared by Pinner's method (Abstr., 1895, i, 137), crystallises from dilute alcohol in white needles melting at 228°. The *potassium* salt crystallises in long needles, and is readily soluble in water, the *ammonium* salt forms leaflets, and the *barium* salt crystallises from alcohol in thin, quadratic plates. The *methylic* salt crystallises from dilute alcohol in long needles, and melts at 93°; the *ethylic* salt also forms long needles, and melts at 62°.

Nitroanisenyltetrazotic acid is obtained by heating anisenyltetrazotic acid with nitric acid (sp. gr. = 1·4) in boiling water for $1\frac{1}{2}$ minutes, and pouring the liquid into cold water after an interval of ten minutes; it crystallises from hot water in long, yellow needles containing $1H_2O$, and melts at 203°. The *barium* salt crystallises from water in

plates, and contains $3H_2O$. *Amidoanisenyltetrazotic acid*, prepared by reducing the nitro-acid with stannous chloride and hydrochloric acid, crystallises from hot water in needles containing $1H_2O$ and melts at 223°. The *hydrochloride* forms needles containing $1H_2O$, and the *potassium* salt crystallises in long needles containing $1H_2O$.

M. O. F.

Etherification of Mono-substituted Benzoic Acids. By VICTOR MEYER (*Zeit. physikal. Chem.*, 1897, **24**, 219—220).—The author had previously stated, as a general law, that, in the case of the mono-substituted benzoic acids, the velocity of etherification is least for the ortho-acids, and that their ethereal salts are the most difficult to hydrolyse (Abstr., 1895, ii, 466). The results of Kellas' experiments (following abstract) are in complete accord with this law, and, further, indicate the marked influence of the molecular weight of the acid, in the case of compounds with analogous substituents; thus, chlorobenzoic acid is etherified more rapidly than the brominated compound, and this again more rapidly than the iodo-compound.

L. M. J.

Velocity of Etherification of Mono-substituted Benzoic Acids, and Hydrolysis of their Ethereal Salts. By ALEXANDER M. KELLAS (*Zeit. physikal. Chem.*, 1897, **24**, 221—252). The researches of Meyer (Abstr., 1895, ii, 466) have shown that, in general, ortho-aromatic acids are more rapidly etherified than the corresponding meta- or para-derivatives. The author, therefore, determined the velocity of etherification for a large number of mono-substitution derivatives of benzoic acid in order to prove the general law and determine the influence of temperature, and of the nature of the substituent. The acids employed were, toluic acids, nitro-, chloro-, bromo-, iodo-, and hydroxy-benzoic acids, the three isomerides being used in each case. The effect of the position of the substituent is seen from the accompanying table, which gives the quantity of ethereal salt produced under similar conditions; the vertical sets alone being comparable.

	Cl–.	Br–.	I–.	NO_2–.	CH_3–.	–OH.
Ortho-	35·7	7·0	9·3	4·2	28·4	15·3
Meta-	55·2	18·4	28·3	22·3	63·8	55·9
Para-	53·1	17·2	26·8	22·3	71·0	51·3

Experiments were then made at a series of temperatures varying from 0° to 51°; the velocity was found to increase with temperature, and tables and curves are given for each acid, the curve in all cases being convex to the temperature axis and considerably steeper for the meta- and para- than for the ortho-derivatives, so that the values approach at 0°. To determine the influence of the substituent, simultaneous experiments were made with various acids, equivalent quantities being used; the order of the velocities was found to be benzoic, chlorobenzoic, toluic, bromobenzoic, iodobenzoic, nitrobenzoic

for the ortho-compounds, but toluic acid comes before chlorobenzoic acid in the meta- and para-compounds, and the nitro- before the iodo-acid in the meta-compounds; the effect of molecular weight is therefore only comparable for analogous compounds. The order of the velocities of hydrolysis were not found to be the same as, or the reverse of, those of etherification, for, although the chlorbromo- and iodo-derivatives are still in the same order, yet the velocity of hydrolysis of toluic acids is much smaller than that of the iodo-acids, whilst the velocity in the case of the nitro-acid is greater than that of the chloro-derivative. In all cases, however, the velocity is least for the ortho-acids. L. M. J.

Hemipinic Acid, and the Isomeric Alkylic Hydrogen Papaverates. By ALFRED KIRPAL (*Monatsh.*, 1897, **18**, 461—466).—The hemipinic acid of which Ostwald determined the conductivity constant (*Zeit. physikal. Chem.*, 1889, **3**, 268) was in reality meta-hemipinic acid; the true acid, $C_6H_2(OMe)_2(COOH)_2$ [3 : 4 : 1 : 2], which has been prepared from opianic acid, has the conductivity constant $K = 0{\cdot}110$.

Ostwald found that α-methylic hydrogen hemipinate, in which the free COOH group has COOMe on one side of it, and H on the other, has a higher conductivity constant than the β-isomeride, in which the free COOH group has on one side OMe, on the other COOMe. In the case of the corresponding derivatives of papaveric acid,

$$C_6H_3(OMe)_2\cdot CO\cdot C \lessdot \begin{matrix} C(COOH):C\cdot COOH \\ N\cdot CH=\!=CH \end{matrix},$$

that methylic hydrogen salt which has the free COOH in the 4′-position with respect to the nitrogen has a higher constant than the isomeride, where it is in the 3′-position: contrary to expectation, the author says, for reasons which it is not easy to see. These two salts, in more concentrated solutions, have a smaller conductivity than the acid, but at a greater dilution their conductivity becomes greater than that of the acid. The same is true of β-methylic hydrogen hemipinate as compared with hemipinic acid; the α-isomeride, on the other hand, has always a smaller conductivity than the acid. C. F. B.

Behaviour of Acetylgallic Acid and Acetyltannin with Hübl's Reagent. By CARL BOETTINGER (*Chem. Zeit.*, 1897, **21**, 57).—Triacetylgallic acid and pentacetyltannin are scarcely attacked by Hübl's reagent, the former giving an iodine number from 1·2 to 2·4, the latter from 2 to 3·1. These compounds dissolve easily in chloroform, but the acetyltannin which is insoluble in a dilute aqueous solution of sodium carbonate is precipitated from its solution in chloroform by adding Hübl's reagent or alcohol. Since, however, gallic acid and tannin both give large iodine numbers, this reaction would seem to be dependent on the presence of unsubstituted hydroxyl groups. Such being the case, if the composition of gallic acid and tannin be assumed to be represented by formulæ obtained by doubling the ordinary formulæ, then the former might be expected to give a larger iodine number than the latter, which contains only five instead of six hydroxyl groups, and this is in accordance with the fact. But on

this assumption, however, pentacetyltannin would contain a carboxyl group and should be of acid character, whereas it is only slowly attacked and decomposed by dilute sodium carbonate solution. It is evident that Hübl's iodine reaction in the case of gallic acid and tannin cannot be attributed to the same cause as the similar reaction afforded by fats. E. W. W.

Diacyl Anilides. By HENRY L. WHEELER, T. E. SMITH, and C. H. WARREN (*Amer. Chem. J.*, 1897, 19, 757—766).—*Benzenesulphacetanilide*, $C_6H_5 \cdot SO_2 \cdot NPhAc$, obtained by the action of acetic anhydride on sodium benzenesulphanilide, separates from dilute solution in the form of large, colourless monoclinic plates melting at 116·5°. *Benzenesulphopropionanilide*, prepared in a similar manner, separates from alcohol in very large crystals melting at 115°. *Benzenesulphobutyranilide* crystallises in stout prisms melting at 89—90°. *Benzenesulphobenzanilide* forms long, thin, monoclinic needles melting at 114—115°.

Benzenesulph-α-naphthalide, $C_{10}H_7NHSO_2C_6H_5$, prepared by the Baumann-Schotten reaction in the usual manner, crystallises from alcohol in needles melting at 168—169°. The corresponding *β-naphthalide* crystallises in oblong plates or flattened prisms melting at 97°. *Benzenesulphobenzo-α-naphthalide* forms minute crystals melting at 193—194°, and the corresponding *β-compound* fine, white needles melting at 161—162°. As the group $-C\genfrac{}{}{0pt}{}{\lessdot H}{\lessdot O}$ exists in the diacyl anilide, the formyl derivative of the above series has been compared crystallographically with its homologues. The results show that acetyl and propionyl derivatives of benzenesulphanilide exhibit close crystallographic analogy, the compounds being monoclinic, hemimorphic, and pyroelectric, their crystallographic axes and the angle β being similar. On the other hand, bezenesulphoformanilide is orthorhombic, and shows no analogy whatever with these compounds. Moreover, crystals of formanilide showed no analogy with those of acetanilide. A. W. C.

Natural Resins ("Überwallungsharze"). III. By MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1897, 18, 481—509. Compare Abstr., 1895, i, 109).—Pinoresinol, from the resin of *Pinus laricio*, has now been obtained by crystallisation from a concentrated alcoholic solution, in large rhombic prisms [$a : b : c = 0·8689 : 1 : 0·3817$]; it melts at 122°, and is now found to have the composition $C_{19}H_{20}O_6$.

The "Überwallung" resin from pines can also be separated by ether into a soluble α- and an insoluble β-resin, present respectively to the extent of 80 and 20 per cent. The α-resin consists of the pinoresinol salts of paracoumaric and abietic acids, the first of which is present in much larger amount; it also contains a little paracoumaric acid, and some vanillaldehyde, the pinoresinol obtained from it is in all respects identical with that described above, $C_{17}H_{12}O_2(OH)_2(OMe)_2$, and yields the same diacetyl and dimethyl derivatives. A *diethylpinoresinol* was also obtained by acting on the potassium salt with ethylic iodide and methyl alcoholic potash; it melts at 118°. Con-

centrated nitric acid converts pinoresinol in acetic acid solution at $-15°$ into dinitroguaiacol $OH\cdot C_6H_2(OMe)(NO_2)_2$ (Herzig, Abstr., 1883, 464). Bromine, in cooled acetic acid solution, converts it into *dibromoresinol dibromide*, $C_{19}H_{18}Br_4O_6$, which melted at any temperature between 225° and 254°, and was possibly not pure.

The β-resin was purified by dissolving it in alcohol, reprecipitating with very dilute hydrochloric acid, boiling for several days with 10 per cent. alcoholic potash, precipitating with sulphuric acid, redissolving in aqueous potash, precipitating the potassium salt by the addition of solid potassium hydroxide, and decomposing it with very dilute hydrochloric acid. It forms a chocolate-brown powder, has the methyl number 56, and appears to have the composition $C_{30}H_{30}O_6(OMe)_2$; its properties are those of a tannol, whence it is named *pinoresinotannol*. It yields a *benzoyl* derivative when it is treated with 10 per cent. aqueous soda and benzoic chloride, and a *methylic* derivative when it is boiled with methylic iodide and methyl alcoholic potash; it is uncertain, in both cases, whether two or three benzoyl or methyl groups enter the molecule; both the products are brown and amorphous.

The "Überwallungs" resin of the larch contains caffeic acid, vanillaldehyde, and an acid resembling ferulic acid. The resinol, separated from it by the methods used in the case of pinoresinol, is named *lariciresinol*, melts at 164°, and appears to have the composition $C_{16}H_{19}O_5$; it forms a *potassium* derivative, $C_{16}H_{17}K_2O_5 + 2H_2O$. Lariciresinol gives the methyl number 73·5—81·4, but from this it is impossible to decide whether it contains two or three methoxyl groups. When it is boiled with acetic chloride, it forms an *acetyl* derivative, melting at 159°, of which the composition could not be determined satisfactorily; when its potassium salt is boiled with excess of acetic anhydride, a substance is formed which melts at 85°, and appears to be a *triacetyl* derivative. C. F. B.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1897, **297**, 271—312. Compare Abstr., 1897, i, 362, 436).—The first instance of the occurrence of a derivative of methylamine in lichens is afforded by *Sticta fuliginosa* (Dickson), which contains trimethylamine.

Erythric acid has been hitherto found only in *Roccella tinctoria* (Ach.), *R. fuciformis* (Ach.), and *Lecanora* (*Ochrolechia*) *tartarea* (L.); it occurs also in *Parmelia olivetorum* (Nyl.), and in *Evernia furfuracea* (L.), giving rise to the red coloration produced on treating the medulla of these lichens with a solution of bleaching powder.

Evernic acid, first obtained by Stenhouse from *Evernia prunastri* (L.), is only to be found in one variety of this lichen, namely, *var. vulgaris* (Körber), and does not occur in *var. thamnodes* (Flotow), which must be, therefore, regarded as a separate species (*Evernia thamnodes*). This acid has been isolated by the author from *Ramalina pollinaria* (Westr.), and *Evernia thamnodes* also contains divarictic acid, obtained by Hesse from *Evernia divaricata* (L.).

Gyalolechia aurella (Hoffm.) contains callopismic (ethylpulvic) acid, which occurs also in *Callopisma vitellinum* (Ehrh.), *Gasparrinia medians*

(Nyl.), and *Candelaria concolor* (Dickson); when the acid is heated with methylic alcohol in closed tubes at 150—160°, it yields a yellowish-green *methylic* salt.

Rochleder and Heldt's chrysophanic acid occurs in *Gasparrinia cirrhochroa* (Ach.), and in *Callopisma flavovirescens* (Mass.); the same substance has been described as parietin by Thompson, physciacic acid by Paternò, chrysophyscin by Lilienthal, and physcion by Hesse.

The author confirms the observation of Hesse regarding the occurrence of ramalic acid in *Ramalina pollinaria* (Westr.); barbatic acid, hitherto found only in *Usnea barbata* (L.), occurs also in *Usnea longissima* (Ach.).

The presence of usnic acid has been established in the following lichens: *Usnea longissima* (Ach.), *Ramalina polymorpha* (Ach.), *Evernia thamnodes* (Flotow), *E. prunastri* (L.) *var. vulgaris* (Körber), *E. divaricata* (L.), *Parmelia conspersa* (Ehrh.), *Placodium gypsaceum* (Sm.), and *P. chrysoleucum* (Sm.).

Squamaric acid, which occurs in *Placodium gypsaceum* (Sm.), crystallises from alcohol in rosettes of slender, white needles, melting at 262—264°; it is insoluble in water, and dissolves with difficulty in chloroform and cold alcohol. The solution in concentrated sulphuric acid is yellow, and in dilute alkalis yellowish-green, the substance being somewhat soluble in sodium carbonate; the alcoholic solution reddens litmus, and develops a deep red coloration with ferric chloride. Although it resembles psoromic acid in crystalline form, melting point, and solubility, it differs from it in its behaviour towards alkalis, which do not give rise to red salts.

Placodiolin has been isolated from *Placodium chrysoleucum* (Sm.), and crystallises from ether in long, highly lustrous prisms, or in thin plates when quickly crystallised; it melts at 154—156°. It is very soluble in chloroform, but dissolves less readily in ether, benzene, and glacial acetic acid; concentrated sulphuric acid develops a red, and alkalis a yellowish-green coloration. The alcoholic solution is feebly acidic, and does not develop colour with ferric chloride; bleaching powder has no effect on the substance.

In addition to the seven species which have been mentioned in previous papers, zeorin occurs in *Anaptychia speciosa* (Wulfen), and salazinic acid, hitherto recognised in *Stereocaulon salazinum* (Bory), is present in *Alectorea cana* (Ach.), *Parmelia perforata* (Ach.), *P. excrescens* (Arnold), *P. conspersa* (Ehrh.), and *Everniopsis Trulla* (Ach.).

The presence of atranoric acid has been already established in no fewer than thirty-five species of lichens; to this number must be added the six following, *Parmelia olivetorum* (Nyl.), *P. perlata var. excrescens* (Arnold), *P. perforata* (Ach.), *P. Nilgherrensis* (Nyl.), *Evernia prunastri* (L.) *var. vulgaris* (Körber), *Everniopsis Trulla* (Ach., Nyl.).

Hesse's statement (Abstr., 1897, i, 257), that *Candelaria concolor* (Dickson) contains chrysophanic acid is, in the author's opinion, erroneous. M. O. F.

Indolinones, III. By Karl Brunner (*Monatsh.*, 1897, 18, 527—549. Compare Abstr., 1897, i, 100, 438).—When acetic, pro-

pionic, butyric or phenylacetic hydrazide, $C_6H_5\cdot NH\cdot NH\cdot CO\cdot CH_2R$, is heated with four times its weight of recently ignited lime for about an hour at 190—200°, ammonia is evolved and a 3′-R-2′-indolinone,

$$C_6H_4{<}{\begin{matrix}CHR\\NH\end{matrix}}{>}CO,$$

is formed, the yield varying from 70—85 per cent. of the theoretical. When R = H, however, it is necessary to heat to 200—220°, and the yield is only 4·5 per cent. Preliminary experiments have shown that the phenylhydrazide of isopropylacetic acid and the methylphenylhydrazide of phenylacetic acid react in the same way.

2′-Indolinone, from acetic phenylhydrazide, was found to be identical with oxindole prepared by von Baeyer's method (Abstr., 1878, 587). 3′-Methyl-2′-indolinone, from propionic phenylhydrazide, is identical with the atroxindole of Trinius (Abstr., 1885, 529); when crystallised from benzene it melts at 123°, from water at 113°, and each modification is converted into the other by contact with a crystal of the latter. When boiled with excess of acetic anhydride, it yields a *monacetyl* derivative melting at 79°; when it is dissolved in dilute sulphuric acid and heated with excess of bromine-water, a *dibromo*-derivative, $C_6H_2Br_2\colon C_3NH_5O$, melting at 171° is formed; heated with methylic iodide and a methyl alcoholic solution of sodium methoxide in a sealed tube at 110—120°, a 1′-methylindolinone is not formed, but 1′ : 3′ : 3′-trimethyl-2′-indolinone (Abstr., 1896, i, 625, and 1897, i, 100) together with some 3′ : 3′-dimethyl-2′-indolinone (Abstr., 1897, i, 438).

3′-Ethyl-2′-indolinone, from butyric phenylhydrazide, crystallises in monoclinic plates (fundamental angles: 100·110 = 54° 10′; 001·110 = 81° 6′; 001·011 = 51° 16′; β = 74° 47′), melts at 102·5°, and boils at 200—220° under 44 mm., at 320—323° under 742 mm., pressure. Its *monacetyl* derivative melts at 45°; it yields a yellow *dinitro*-derivative melting at 176°, when it is dissolved in acetic acid and the solution warmed with strong nitric acid; it also forms a *dibromo*-derivative, $C_6H_2Br_2\colon C_4NH_7O$, which melts at 150°. Unlike its methyl analogue, it does undergo substitution in the 1′-position when it is heated with methylic iodide and sodium methoxide in methyl alcoholic solution. *1′-Methyl-3′-ethyl-2′-indolinone* boils at 280—285° under 745 mm. pressure; it yields a *bromo*-derivative, melting at 161°, which gives up some, or all, of its bromine when boiled with alcoholic potash, and must therefore contain the bromine in the pyrrolidone, and not in the benzene, ring. *3′-Phenyl-2′-indolinone*, from phenylacetic phenylhydrazide, melts at 183°; it forms a *monacetyl* derivative, melting at 103°, and a *monobromo*-derivative, $C_6H_3Br\colon C_8NH_7O$, melting at 191°.

C. F. B.

Action of Sulphur Chloride on Aromatic Amines. By ALBERT EDINGER (*Ber.*, 1897, **30**, 2418—2420. Compare Abstr., 1897, i, 103).—The compound previously obtained by the action of sulphur chloride on quinoline has the molecular formula $C_{18}H_{10}N_2S_2$ and is very stable towards oxidising agents. Nitric acid converts it into mono- and dicarboxylic acids of pyridine, and it has therefore the constitution $C_9NH_5{<}{\begin{matrix}S\\S\end{matrix}}{>}C_9NH_5$. The substance is not poisonous.

The application of this reaction to a number of aromatic amines has shown that similar compounds are only formed when the amine belongs to the quinoline series, and not when it is a derivative of pyridine, isoquinoline, or hydroxyquinoline.

Orthomethylquinoline, when treated with sulphur monochloride or dichloride, yields a *substance* of the same composition as that obtained from quinoline itself, the methylic group being eliminated; this substance melts above 360° and is converted by nitric acid into nicotinic acid. It is accompanied by halogen derivatives of quinoline: 1 : 3-dichloroquinoline melting at 104°, and a tetrachloroquinoline melting at 121°. Orthohydroxyquinoline only yields a dichloro-compound melting at 179°; parahydroxyquinoline, a monochloro-compound melting at 187°, and isoquinoline, a trichloro-compound melting at 124°, no sulphur compound being formed. It has not been found possible to obtain any pure product by the application of the reaction to pyridine.

A. H.

Additive Compounds and Substitution Derivatives of Phenyldimethylpyrazolone. By M. C. Schuyten (*Chem. Zeit.*, 1897, **21**, 11).—By the action of nitrous acid, that is, of a solution of sodium nitrite with glacial acetic acid, on the additive compounds of antipyrine with thiocyanic acid, cadmium chloride, zinc chloride, resorcinol, salicylic acid and chloral hydrate respectively, the bluish-green coloration characteristic of the nitroso-derivative was produced, except in the case of the resorcinol compound, which gave a yellow solution. In every case, however, more or less speedy decomposition followed and no nitroso-derivative could be isolated. From the products of the reaction with the zinc chloride compound, a yellow, flocculent precipitate which became black at 185°, and decomposed with violence at 188°, and a dark red powder were obtained. Similar negative results were obtained by passing nitric oxide gas over the above-mentioned additive compounds or their solutions. Attempts to prepare additive compounds of nitroso-antipyrine analogous to those of antipyrine also failed.

E. W. W.

Action of Bases on Aposafranine. By Otto Fischer and C. Giesen (*Ber.*, 1897, **30**, 2489—2494. Compare Abstr., 1896, i, 323).—By heating aposafranine hydrochloride with methylamine hydrochloride and methylamine in alcoholic solution for 5—6 hours at 100°, *methylamidosafranine*, $\begin{matrix}NHMe\\NH\end{matrix}\!\!>\!C_6H_2\!<\!\!\begin{matrix}N\\NPh\end{matrix}\!\!>\!C_6H_4$, is obtained; its *hydrobromide*, $C_{19}H_{16}N_4,HBr$, was analysed. Solutions of the salts are orange coloured, but are turned pink by the addition of strong acids; the iodide is only sparingly soluble. With paranisidine, green, crystalline *paranisidoaposafranine*, $C_{25}H_{20}N_4O$, is formed; solutions of this are brown; the *hydrochloride* is yellowish-green. With ethylenediamine in boiling alcoholic solution, the product is a brown, crystalline substance with bluish-green surface-lustre,

$$C_{20}H_{16}N_4\ \ (?NH_2\cdot CH_2\cdot CH_2\cdot N{:}C_6H_2\!<\!\!\begin{matrix}N\\NPh\end{matrix}\!\!>\!C_6H_4),$$

which forms orange-red solutions, coloured violet by mineral acids.

When it is heated, best with mercuric oxide, or when aposafranine is heated with ethylenediamine at 150—160°, a brownish-yellow, crystalline substance with a greenish surface-lustre is obtained; the alcoholic solution is turned first red and eventually blue by the addition of mineral acids; the solution in benzene has a greenish-yellow fluorescence. The substance yields a mon-acetyl derivative and is possibly $CH_2<{NH \atop CH_2\cdot N}>C_6H_2<{N \atop NPh}>C_6H_4$.

With orthamidophenol, aposafranine yields a brownish-red crystalline substance, possibly $C_6H_4<{O \atop N}>C_6H_2<{N \atop NPh}>C_6H_4$; this forms a cherry-red solution in alcohol, with a blood-red fluorescence. Naphthyleneorthodiamine also reacts with aposafranine. C. F. B.

A New Cyclic Compound. By MILORAD Z. JOVITSCHITSCH (*Ber.*, 1897, **30**, 2426—2431).—A substance having a ring formation differing only from that of the peroxides in that it contains a nitrogen atom in place of carbon and that the two remaining nitrogen atoms are directly joined, is formed when the aniline derivative of ethylic oximidoacetate is treated with nitrous acid; that this substance is in reality represented by the formula $\begin{matrix} COOEt\cdot CH—N—O \\ | \quad\quad | \quad\ | \\ NPh—N—O \end{matrix}$ is deduced from the fact that of the only other two possible formulæ,

NO·NPh·C(NOH)·COOEt and NO·NPh·CH(NO)·COOEt,

the former is improbable, since hydroxylamine is not eliminated when the substance is heated as in Liebermann's reaction, and the latter owing to the fact that no amido-derivative is formed on reduction; the *aniline derivative of ethylic oximidoacetic acid*, NHPh·C(NOH)·COOEt, is formed by the action of aniline on ethylic chloroximeacetic in alcoholic solution, and crystallises from hot dilute alcohol in long, slender prisms melting at 109°; it is nearly insoluble in cold water, but dissolves readily in alcohol and ether; the action of the calculated quantity of potassium nitrite and sulphuric acid, on an ethereal solution of this ethylic salt, gives rise to the cyclic compound above mentioned, which, after the addition of the sulphuric acid, separates from the solution in slender, orange-yellow crystals which decompose at 169°; its solution in dilute alkali is coloured deep violet, gradually changing to deep red when boiled, owing to the elimination of the carbethoxy-group and formation of the dialkali salt of the *substance* $\begin{matrix} CH_2—N—O \\ | \quad\ | \quad | \\ NPh—N—O \end{matrix}$ for which, as also for its carbethoxy-derivative, the author does not attempt to propose a name; the free substance, which can be separated by acidifying, crystallises from dilute alcohol in slender needles containing $1H_2O$, which it loses at 140—190°, finally decomposing at 206°. The red alkali salt loses its colour on prolonged exposure to the air, and almost instantly in the presence of carbonic anhydride. A *substance*, $C_{14}H_{18}N_2O_3$, is also formed by the action of nitrous acid on the aniline derivative; this crystallises from water in slender, yellow, fluorescent prisms melting at 69—70°. J. F. T.

Phenyltriazoles. II. By ASTRID CLEVE (*Ber.*, 1897, **30**, 2433—2438).—A continuation of a former paper in which the preparation of phenyltriazoles from Widman's 3-hydroxy-1-phenyl-1 : 2 : 4-triazoles by substitution with chlorine and subsequent reduction with hydriodic acid and red phosphorus, was described (Abstr., 1897, i, 172).

3-*Chloro*-1-*phenyl*-5-*propyl*-1 : 2 : 4-*triazole*, $\begin{matrix}\mathrm{CCl{=}N} \\ \mathrm{N{:}CPr^{\alpha}}\end{matrix}\!\!>\!\mathrm{NPh}$, is a tolerably mobile oil boiling at 322·5°, and having a sp. gr. = 1·1884; it does not yield salts with acids, but on distillation is partially converted into its *hydrochloride* which separates in glistening scales.

1-*Phenyl*-5-*propyl*-1 : 2 : 4-*triazole*, $\begin{matrix}\mathrm{CH{=}N} \\ \mathrm{N{:}CPr^{\alpha}}\end{matrix}\!\!>\!\mathrm{NPh}$, formed from the above by reduction, is a colourless oil boiling at 285—286°, and of sp. gr. = 1·0827. The *mercurochloride* crystallises from alcohol in colourless prisms melting at 111—112°.

3-*Chloro*-1-*phenyl*-5-*butyl*-1 : 2 : 4-*triazole*, $\begin{matrix}\mathrm{CCl{=}N} \\ \mathrm{N{:}C(C_4H_9)}\end{matrix}\!\!>\!\mathrm{NPh}$, is a pale yellow oil boiling at 327—328° (corr.), and of sp. gr. = 1·1547; on reduction, it yields 1-*phenyl*-5-*butyl*-1 : 2 : 4-*triazole*, an oil boiling at 288—289°, and yielding a *picrate* crystallising from dilute alcohol in needles melting at 136°, and a *mercurochloride* consisting of colourless prisms melting at 116°.

3-*Chloro*-1-*phenyl*-5-*phenylchlorethyl*-1 : 2 : 4-*triazole*,

$$\begin{matrix}\mathrm{CCl{=}N} \\ \mathrm{N{:}C(C_2H_3PhCl)}\end{matrix}\!\!>\!\mathrm{NPh},$$

which is produced when hydroxyphenylstyryltriazole is treated with phosphorus pentachloride, consists of flat needles melting at 112—113°; on reduction, it yields 1-*phenyl*-5-*phenylethyl*-1 : 2 : 4-*triazole*, $\begin{matrix}\mathrm{CH{=}N} \\ \mathrm{N{:}C(C_2H_4Ph)}\end{matrix}\!\!>\!\mathrm{NPh}$, a colourless oil boiling at 340—350°, the *platinochloride* forms yellowish-red crystals decomposing at 180—190°.

1-*Phenyl*-5-*styryl*-1 : 2 : 4-*triazole*, $\begin{matrix}\mathrm{CH{=}N} \\ \mathrm{N{:}C(CH{:}CHPh)}\end{matrix}\!\!>\!\mathrm{NPh}$, prepared from phenylphenyethyltriazole by treating it with bromine, separates from a mixture of light petroleum and benzene in colourless prisms melting at 119—120°. The *hydrochloride* consists of colourless needles, the *platinochloride* of yellowish-red leaflets, whilst the *picrate* separates from alcohol in yellow prisms melting at 167°. 1-*Phenyl*-5-*phenyldibromethyl*-1 : 2 : 4-*triazole*, which is an intermediate product in this reaction, forms silky needles melting at 152°. J. F. T.

Action of Hydrazine on Imido-ethers. By ADOLF PINNER (*Annalen*, 1897, **297**, 221—271. Compare Abstr., 1897, i, 637, and 1894, i, 385).—The author discusses at some length the action of hydrazine derivatives on imido-ethers. The experimental portion of the paper has been already published (*loc. cit.*). M. O. F.

Action of Hydrazine on Imido-ethers. By ADOLF PINNER (*Annalen*, 1897, **298**, 1—53. Compare foregoing abstract).—The

hydrochloride of paratolenylhydrazidine (Abstr., 1895, i, 136) forms lustrous, colourless prisms. *Tolyltetrazole* is the compound described as paratolyltetrazotic acid (*loc. cit.*), obtained by the action of nitrous acid on paratolenylhydrazidine.

[With C. GÖBEL.]—The compounds dealt with in this portion of the paper have been already described (Abstr., 1897, i, 639).

[With JAMES COLMAN.]—*Dihydroxybenzyldihydrotetrazine*,

$$OH\cdot CHPh\cdot C\underset{N\text{———}N}{\overset{NH\cdot NH}{\lessgtr}}C\cdot CHPh\cdot OH,$$

is obtained by the action of hydrazine on the imido-ether prepared from mandelonitrile, it not having been found possible to produce the intermediate hydrazidine derivative; it crystallises from alcohol in yellowish needles and melts at 193°. Hydrochloric acid resolves the substance into benzaldehyde, formic acid, and hydrazine hydrochloride. The *tetracetyl* derivative forms colourless crystals and melts at 203°.

Furfuryltetrazole is the name now given to furfuryltetrazotic acid (Abstr., 1895, i, 270).

[With ALFRED SALOMON.]—The compounds enumerated in this portion of the paper have been already described (Abstr., 1897, i, 638).

[With FELIX GRADENWITZ.]—*Paranitrobenzimido-ether*,

$$NH\colon C(C_6H_4\cdot NO_2)\cdot OEt,$$

crystallises in stellar aggregates of needles and melts at 78°. The *hydrochloride* forms large, lustrous prisms and melts at 197°, yielding ethylic chloride and paranitrobenzamide; water converts it into ammonium chloride and ethylic paranitrobenzoate. The *platinochloride* crystallises in lustrous, yellow needles, and melts at 141°; the *sulphate* is unstable, and crystallises in needles.

Paranitrobenzamidine, $NH\colon C(C_6H_4\cdot NO_2)\cdot NH_2$, arises from the action of ammonia on the imido-ether; it crystallises in needles, and melts at 215°. The *hydrochloride* forms highly refractive, rhombic needles. *Acetoparanitrobenzamide*, $NO_2\cdot C_6H_4\cdot CO\cdot NHAc$, produced when the hydrochloride of the imido-ether is heated with sodium acetate and acetic anhydride, crystallises from alcohol in six-sided plates, and melts at 165°.

Paranitrobenzenylhydrazidine, $NH_2\cdot N\colon C(NH_2)\cdot C_6H_4\cdot NO_2$, is obtained by the action of hydrazine on the imido-ether, and crystallises from alcohol in lustrous, reddish needles melting at 195°. The *picrate* crystallises in yellow needles, and melts at 177°.

Paranitrophenyltetrazole, $NO_2\cdot C_6H_4\cdot C\underset{N—N}{\overset{NH\cdot N}{\lessgtr}}$, is produced by the action of nitrous acid on the hydrazidine, and crystallises from alcohol in white needles; it melts and becomes red at 219°.

Diparanitrobenzenylhydrazidine,

$$NH_2\cdot C(C_6H_4\cdot NO_2)\colon N\cdot N\colon C(C_6H_4\cdot NO_2)\cdot NH_2,$$

is obtained by the action of alcoholic hydrazine (1 mol.) on the imido-ether ($1\frac{1}{2}$ mols.) and forms small, reddish, rhombic crystals insoluble in common solvents; it darkens at 220°, and melts at 257°. The *hydrochloride* yields diparanitrophenyltriazole when heated; the *nitrate* melts and effervesces at 143°.

Diparanitrophenyltriazole, $NO_2\cdot C_6H_4\cdot C{\lessgtr}^{NH}_{N\cdot N}{\gtrless}C\cdot C_6H_4\cdot NO_2$, is prepared by heating the hydrazidine with glacial acetic acid, and crystallises from alcohol in colourless needles melting at 257°. The *acetyl* derivative also forms colourless needles and melts at 237°.

Diparanitrophenyldihydrotetrazine,

$$NO_2\cdot C_6H_4\cdot C{\lessgtr}^{NH\cdot NH}_{N\text{——}N}{\gtrless}C\cdot C_6H_4\cdot NO_2,$$

is obtained from the imido-ether (1 mol.) and hydrazine ($1\frac{1}{2}$ mols.) in somewhat less concentrated solution; it forms red needles soluble in alcohol, benzene, and acetone, and melts at 215°.

Diparanitrophenyltetrazine, $NO_2\cdot C_6H_4\cdot C{\lessgtr}^{N:N}_{N\cdot N}{\gtrless}C\cdot C_6H_4\cdot NO_2$, is produced on oxidising the foregoing compound; it crystallises in flat, red needles, and melts at 218°. M. O. F.

Action of α-Brominated Acids and Ketones on Orthamidothiophenol. By OSKAR UNGER and G. GRAFF (*Ber.*, 1897, **30**, 2389—2399. Compare Abstr., 1897, i, 302).—Ketodihydrobenzoparathiazine is also formed by the action of ethylic chloracetate on amidothiophenol. When treated with aqueous potash, glistening crystals of *potassium orthamidophenylthioglycollate*,

$$NH_2\cdot C_6H_4\cdot S\cdot CH_2\cdot COOK,$$

are formed. Nitrous acid yields a diazo-salt which yields a colouring matter with β-naphthol. The thiazine compound is converted by oxidation into a *compound* which melts indefinitely between 140° and 150° and yields a *phenylhydrazone*, crystallising in yellow needles and melting at 137°. When distilled with zinc dust, the thiazine yields a small quantity of indole.

α-Methylketodihydrobenzoparathiazine, $C_6H_4{<}^{S\text{—}CHMe}_{NH\cdot CO}$, obtained by the action of α-bromopropionic acid on amidothiophenol, crystallises in concentrically grouped needles melting at 128°. The *ethyl* derivative is prepared by means of α-bromobutyric acid, and crystallises in porcelain white prisms melting at 105—106°, whilst *α-phenylketodihydrobenzoparathiazine*, $C_6H_4{<}^{S\text{—}CHPh}_{NH\cdot CO}$, is obtained from phenylbromacetic acid and crystallises in colourless needles melting at 204°. Ethylic α-chloracetacetate reacts with orthamidothiophenol to form a compound, $C_{12}H_{13}NO_2S$, which crystallises in slender, golden yellow needles and melts at 145°; it dissolves in hydrochloric acid, yielding a solution which, on treatment with sodium nitrite, forms phenylene diazosulphide. When heated with phenylhydrazine on the water bath, it yields diamidodiphenylic bisulphide and 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone. The condensation product is completely decomposed by aqueous potash, yielding a *compound* which crystallises in colourless needles melting at 159°. Its composition has not yet been ascertained.

Bromacetic bromide reacts with orthamidothiophenol to form a substance of the composition $C_{14}H_{12}N_2S_2$, its molecular weight as determined by the boiling point method being about 272. It has

decided basic properties, and yields a diazo-salt with sodium nitrite. As it yields benzothiazole on oxidation with potassium permanganate, it is probable that the original compound has the constitution $C_6H_4<{}^{S}_{N}>C\cdot CH_2\cdot S\cdot C_6H_4\cdot NH_2$. A. H.

Synthesis of Heteroxanthine and Paraxanthine. By Emil Fischer (*Ber.*, 1897, 30, 2400—2415. Compare Abstr., 1897, i, 641, and this vol., i, 48).—Theobromine is converted by a mixture of phosphorus oxychloride and pentachloride into 7-methyltrichloropurine, but when it is heated with the oxychloride alone, the chlorination does not proceed so far and 2 : 6-*dichloro*-7-*methylpurine*,

$$\begin{array}{l} N{:}CCl\cdot C\cdot NMe \\ CCl{:}N\cdot C \text{——} N \end{array}\!\!>CH,$$

is produced; this crystallises in slender, colourless needles, melting at 199—200° (corr.), and is only sparingly soluble in water. Phosphorus pentachloride at 170° converts it into trichloromethylpurine. When it is heated with hydrochloric acid (sp. gr. 1·19) at 120—125°, it yields the *hydrochloride* of 7-methylxanthine, which crystallises in almost colourless prisms. The free base $\begin{array}{l} NH\cdot CO\cdot C\cdot NMe \\ CO\cdot NH\cdot C \text{——} N \end{array}\!\!>CH$, is identical with heteroxanthine; this has no definite melting point, but softens at 360° and melts and decomposes at 380°; when quite pure, it dissolves in 142 parts of boiling water, the greater solubility found by Bondzyński and Gottlieb (Abstr., 1895, i, 434) being probably due to the presence of a small amount of impurity. 2 : 6-Dichloro-7-methylpurine is converted by sodium ethoxide into a compound which is most probably 2-*chloro*-6-*ethoxy*-7-*methylpurine*,

$$\begin{array}{l} N{:}C(OEt)\cdot C\cdot NMe \\ CCl{:}N \text{——} C \text{——} N \end{array}\!\!>CH;$$

this dissolves in about 800 parts of boiling water and crystallises in slender needles which melt and decompose at about 240°; hydrochloric acid converts it into heteroxanthine. 2-*Chloro*-6-*oxy*-7-*methylpurine* is obtained by warming dichloromethylpurine with an aqueous alkali and is best purified by means of the *barium* salt, which crystallises in slender prisms. The compound, which crystallises in short prisms and commences to decompose at 310°, dissolves in about 150 parts of boiling water or 250 parts of boiling alcohol. 2-*Chloro*-6-*oxy*-1 : 7-*dimethylpurine*, $\begin{array}{l} NMe\cdot CO\cdot C\cdot NMe \\ CCl{:}N\cdot C \text{——} N \end{array}\!\!>CH$, is prepared by the action of aqueous potash and methylic iodide on chloroxymethylpurine; it dissolves in about 50 parts of boiling water and melts and decomposes at about 270° when rapidly heated. 1 : 7-Dimethylxanthine or paraxanthine, $\begin{array}{l} NMe\cdot CO\cdot C\cdot NMe \\ CO\cdot NH\cdot C \text{——} N \end{array}\!\!>CH$, obtained by heating the foregoing compound with hydrochloric acid of sp. gr. 1·19 at 125—130°, is identical with the paraxanthine isolated by Salomon from urine (Abstr., 1883, 601; 1886, 266); when treated with potash and methylic iodide, it is converted into caffeine.

2-Chloro-6-oxy-7-methylpurine, on reduction with hydriodic acid, yields

6-*oxy*-7-*methylpurine* (7-methylhypoxanthine), $\begin{matrix}\mathrm{NH\cdot CO\cdot C\cdot NMe} \\ \mathrm{CH{:}N-C---N}\end{matrix}\!\!>\!\mathrm{CH}$, which crystallises in slender, colourless needles, melts at about 355° when rapidly heated, and is readily soluble in hydrochloric and sulphuric acids. The *nitrate* forms large, compact crystals; the *platinochloride* is readily soluble in hot water, the *aurochloride* more sparingly; the *silver* salt is a fine, white, crystalline powder. On methylation, the base yields dimethylhypoxanthine. 2-*Amido*-6-*oxy*-7-*methylpurine* (7-methylguanine), $\begin{matrix}\mathrm{NH——CO\cdot C\cdot NMe} \\ \mathrm{C(NH_2){:}N\cdot C{=\!=}N}\end{matrix}\!\!>\!\mathrm{CH}$, is obtained by the action of ammonia on chloroxymethylpurine, and crystallises in slender, colourless needles which decompose at about 390°; it readily forms crystalline salts with acids, the *hydrochloride, sulphate, nitrate, platinochloride* and *aurochloride* having been prepared. It also dissolves in cold dilute alkalis, but is reprecipitated by carbonic anhydride. The *sodium* salt crystallises in very slender needles, whilst the *silver* salt is an amorphous precipitate. When treated with hydrochloric acid and potassium chlorate, it yields guanidine. 2-*Amido*-6-*oxy*-1 : 7-*dimethylpurine* (1 : 7-dimethylguanine), $\begin{matrix}\mathrm{NMe\cdot CO\cdot C\cdot NMe} \\ \mathrm{NH_2\cdot C{=\!=}N---C---N}\end{matrix}\!\!>\!\mathrm{CH}$, obtained by the action of ammonia on chloroxydimethylpurine, separates from water in crystals which contain water of crystallisation, but become anhydrous at 100° and then melt at 343—345° (corr.). The *nitrate* crystallises in plates, the *hydrochloride* and *sulphate* in needles. The *platinochloride* and *aurochloride* are both sparingly soluble. Potassium chlorate and hydrochloric acid convert it into methylguanidine.

A. H.

Non-nitrogenous Decomposition Products of Morphine. By EDUARD VONGERICHTEN (*Ber.*, 1897, 30, 2439—2444).—Bromomorphenol methyl ether, is formed when bromomethylmorphimethinmethyl iodide, is heated with concentrated sodium hydroxide solution under certain conditions, the yield being about 10 per cent. On oxidation with chromic acid, it does not yield a phenanthraquinone derivative, but is converted into a substance melting above 315° and crystallising from quinoline in glistening, reddish-brown needles having the same empirical formula as the original brominated ether. On reduction, it yields the corresponding *morphenol*, $C_{14}H_7O\cdot OH$, which crystallises from alcohol or ether in needles and melts at 135°. The *acetate* crystallises from alcohol and acetic acid in white needles.

From these and other considerations, the author considers the formula of the compound $C_{14}H_8O$ to be either $\begin{matrix}\mathrm{C_6H_4\cdot C_6H_4\;\; C_6H_4\cdot C_6H_4} \\ \mathrm{CO-C{=\!=}C---CO}\end{matrix}$ or $\mathrm{O}\!<\!\begin{matrix}\mathrm{C_6H_3\cdot C_6H_4\;\; C_6H_4\cdot C_6H_3} \\ \mathrm{C{=\!=}C——C{=\!=}C—}\end{matrix}\!\!>\!\mathrm{O}$.

J. F. T.

Specific Rotatory Power of β-Glutin. By FRIEDRICH FRAMM (*Pflüger's Archiv.*, 1897, 68, 144—167).—β-glutin is strongly lævorotatory and shows no birotation. Numerous tables are given showing the effect on the rotation of concentration, temperature, and the influence of various reagents, salts, acids, and alkalis. W. D. H.

Halogen Derivatives from Proteids. By F. GOWLAND HOPKINS and FRANCIS W. BROOK (*J. Physiol.*, 1897, **22**, 184—197).—The halogens are effective reagents for the precipitation of proteids, the present paper relating to the precipitates obtained from diluted egg white. The substances obtained, which resemble proteids in being indiffusible and of high molecular weight, give the xanthoproteic and violet biuret reactions; after gastric digestion, they give a pink biuret reaction. They are soluble in dilute alkaline solutions, from which they are precipitable by acetic acid. They differ from proteids in not giving Millon's reaction, and in being soluble in absolute alcohol; the iodine derivative is least soluble in alcohol. From their alcoholic solutions, they are precipitated by the addition of ether, the substance thus obtained containing a higher percentage of halogen than that precipitated by acid from an alkaline solution. Thus:

	Chlorine per cent.	Bromine per cent.	Iodine per cent.
Product after treatment with sodium carbonate	(3·6 and) 1·89	3·92	6·28
Product precipitated from alcoholic solution	6·07	14·89	

Taking the lower series, the bromine percentage is very nearly the mean of the chlorine and iodine percentages, in accordance with the relation that holds between the atomic weights of the halogens. It is believed that, after treatment with alkalis, one has to deal with substituted bromine, whereas after treatment with alcohol there is additive bromine as well. Since aromatic substances like tyrosine no longer give Millon's reaction when halogen has entered the ring, it seems probable that, in these derivatives of proteid, the halogen has entered an aromatic nucleus in the proteid molecule. The halogen derivatives of proteid yield no trace of lead sulphide when heated with alkaline solutions of lead salts; the sulphur is still all present, but probably in a sulphonic or other oxidised group. Efforts to obtain the original proteid from the halogen derivatives have hitherto proved fruitless.

W. D. H.

The Biuret Reaction of Albumin. By HUGO SCHIFF (*Chem. Zeit.*, 1897, **21**, 55—56).—In answer to Loew's criticism (*Chem. Zeit.*, 1896, **20**, 1000), that the anhydride of aspartic acid gives the biuret reaction, whereas, according to the author's theory, it should not do so, the author points out that the composition of this anhydride is unknown, since it is derived from 4 to 8 molecules of aspartic acid. It is characteristic, however, that aspartic acid does not give this reaction, whilst asparagine gives a reaction very similar to the biuret reaction, the coloration being only a little more bluish-violet. The product obtained by the action of formaldehyde and hydrochloric acid on albumin, which is insoluble in water and alkalis, gives the biuret reaction, for fragments of it placed in the almost colourless solution

become reddish-violet after a time. Moreover, Blum's solution of albumin (Abstr., 1896, 658), prepared by the action of formaldehyde alone, although it does not coagulate on heating, also gives this reaction. If this substance is a methylene-albumin, then, according to the author, it does not contain the symmetrical group, $\begin{matrix}-NH\\-NH\end{matrix}\!\!>\!CH_2$, for derivatives of biuret, oxamide, and malonamide in which two hydrogen atoms of each amido-group are symmetrically substituted do not give the biuret reaction. E. W. W.

Precipitation of Caseinogen, a Simple Means of Estimating Acidity. By Paul Grützner (*Pflüger's Archiv.*, 1897, **68**, 168—175).—When milk is added gradually to various acids, the precipitate which first forms redissolves on shaking it up. The first appearance of a permanent precipitate is a measure of the strength and acidity of the acid; the stronger acids need much more milk for this purpose, and precipitate more caseinogen than the weaker ones, thus a molecule of hydrochloric acid in dilute aqueous solution precipitates five or six times as much caseinogen as a molecule of acetic acid.

W. D. H.

Decomposition Products of Carniferrin. By Paul Balke (*Zeit. physiol. Chem.*, 1896, **22**, 248—264. Compare Siegfried, Abstr., 1895, i, 76 and 313).—It is shown that Siegfried's carnic acid is identical with Kühne's antipeptone, considerable quantities of which the author prepared by a method differing somewhat from that described by Kühne; both compounds give similar numbers on analysis and yield identical salts. By the oxidation of barium carnate (1 equivalent) with barium permanganate (1 equivalent) at temperatures below 5°, a new acid, *oxycarnic acid*, $C_{30}H_{41}N_9O_{15}$, is obtained; it is best purified by evaporating its aqueous solution to a syrup, then pouring it into alcohol, and washing the precipitate successively with alcohol and with ether. The *zinc* salt, $C_{30}H_{39}N_9O_{15}Zn$; *barium* salt, $C_{30}H_{39}N_9O_{15}Ba$, and *silver* salt, $C_{30}H_{38}N_9O_{15}Ag_3 + 2H_2O$, are described. The *acid* itself is a snow-white, hygroscopic powder, readily soluble in water, sparingly in alcohol, and insoluble in ether. It reddens blue litmus, is capable of decomposing carbonates, and gives precipitates with picric, phosphotungstic, and tannic acids, but not with lead acetate, acetic acid, or potassium ferrocyanide.

Siegfried has shown that carniferrin obtained from milk has the same percentage composition as that obtained from meat extract, but that when hydrolysed with barium hydroxide it yields, besides lactic and succinic acids, an acid closely related to carnic acid, which he termed orylic acid. According to the author, orylic acid has the composition $C_{18}H_{28}N_4O_8$. When dry, it is a yellowish-white powder, which is extremely hygroscopic and, when freshly prepared, readily soluble in water; it is sparingly soluble in alcohol but insoluble in ether, and is a strong dibasic acid, resembling carnic acid. The *zinc* salt, $C_{18}H_{26}N_4O_8Zn$, and *silver* salt, $C_{18}H_{25}N_4O_8Ag_3 + 3H_2O$, are described. When heated with hydrochloric acid at 130°, orylic acid yields leucine as one of its decomposition products. J. J. S.

Organic Chemistry.

Determination of the Number of Isomeric Paraffins of the Formula C_nH_{2n+2}. By FELIX HERRMANN (*Ber.*, 1897, **30**, 2423—2426). —The author describes in outline a somewhat simpler method than those adopted by Cayley and Losanitsch for the determination of the number of isomeric paraffins of the formula C_nH_{2n+2}. H. C.

Decomposition of Heptane and Octane at High Temperatures. By R. A. WORSTALL and A. W. BURWELL (*Amer. Chem. J.*, 1897, **19**, 815—845).—For this investigation, ordinary crude 63° naphtha of sp. gr. = 0·7310 at 15°, consisting practically of heptane and octane, was employed; the greater portion passed over between 100° and 120°. When gas was manufactured from this material by the Pintsch process, the tar which condensed in the hydraulic main was equivalent to about 25 per cent. of the oil used; it had a sp. gr. = 0·9369 at 15°; by the action of bromine, 34·48 per cent. was added, and 18·88 per cent. substituted. It was found that 100 parts of heptane and octane yielded 25 parts of methane, 26 of olefines, 13 of acetylene, 12·5 of benzene, 3·0 of toluene, 3·0 of xylenes, &c. (120—200°), 4·5 of aromatic hydrocarbons (200—300°), 2·3 of aromatic hydrocarbons (above 300°), 3·6 of naphthalene, 1·3 of anthracene, 0·1 of phenanthrene, 0·1 of chrysene, about 0·01 of fluoranthrene (?), 0·01 of phenols. Naphthenes, thiophen, and diphenyl were absent, and no paraffins other than the original heptane and octane were present.

About 10 per cent. of a liquid was deposited during the compression of the gas under 15 to 17 atmospheres. This consisted of hydrocarbons of low boiling point, about 6 per cent. being unsaturated hydrocarbons boiling at 20—78°, 80 per cent. benzene, and 10 per cent. toluene and xylene, but no paraffins other than the original heptane and octane were present. The gas was made up of 11·8 per cent. of nitrogen, 11·3 of acetylene (and ethylene ?), 15·5 of other illuminants, 18·4 of hydrogen and 42·9 of methane. 1000 cubic feet of gas was obtained from 16 gallons of oil.

It would seem, judging from these results, and those described by Letny, by Berthelot, and by Norton and Noyes, that all hydrocarbons, under similar conditions of temperature, yield the same products. If such is the case, then Schulze's theory of the formation of coal-tar hydrocarbons from phenols cannot be correct. Similarly, explanations such as those of Berthelot and Haber, which assume that the paraffins first split up into simpler molecules, are confronted by the facts that these lower hydrocarbons are not found among the products, and that hydrocarbons which do not belong to the paraffin group yield the same products as the paraffins. E. W. W.

Composition of Scottish Paraffin Oil. By FRIEDRICH HEUSLER (*Ber.* 1897, **30**, 2743—2752).—The fraction boiling below 110° contains paraffins, 42 per cent.; naphthenes, 10; aromatic hydrocarbons, 7·3, and

ethylene, &c., 39 ; the paraffins and naphthenes were determined in the manner described below, the aromatic hydrocarbons as dinitrotoluene ; the total amount of saturated hydrocarbons was also determined by boiling some of the sample for 1 hour with about 7·5 per cent. of aluminium chloride and distilling over the hydrocarbons with steam. In the case of Saxon lignite, the corresponding numbers were 16, 4, 45, and 31 per cent. The small quantity of aromatic hydrocarbons found in this may have been formed by pyrogenic reactions from the fatty hydrocarbons present, but this cannot be true of the much larger quantity contained in the Scotch oil, since only a small amount of benzene would be formed at the comparatively low temperature of the retorts in which the shale is distilled. The Scotch paraffin shale then, unlike the Saxon lignite, probably contains considerable quantities of aromatic compounds ready formed ; it is, further, most probably of animal origin, whilst the lignite is vegetable.

The paraffins in the oil boiling below 180° were estimated by treating a sample with cooled fuming nitric acid, and measuring the residue ; it amounted to 40—44 per cent., boiled at 149—154°, had sp. gr. = 0·730 at 15°, and contained C, 84·4 ; H, 15·8 per cent., which agrees well with C_9H_{20}. The paraffins and naphthenes were separated in company by treating the oil successively with somewhat diluted sulphuric acid, strong sulphuric acid, and fuming sulphuric acid ; the residue was fractionated, and the analyses and specific gravities of the fractions showed that they contained about 20 per cent. of naphthenes. The presence of benzene, toluene, metaxylene, and cumene, and the absence of naphthalene, were also proved. Ethylene hydrocarbons were separated by adding bromine until immediate decolorisation no longer ensued ; the chief fraction of the bromides formed (from the fraction of the oil boiling at 60—70°) boiled at 87—95° under 15—16 mm. pressure, had a sp. gr. = 1·623 at 15°, and contained C, 29·1 ; H, 4·8 ; Br, 66·2 (between $C_5H_{10}Br_2$ and $C_6H_{12}Br_2$, and nearer the latter). The nitriles of fatty acids were detected by boiling the oil with solid caustic potash ; the solid product was separated from the oil, and dissolved in water ; pyrrolines were driven off by steam-distillation, and the phenols removed after saturation with carbonic anhydride, the fatty acids being then set free with sulphuric acid. These, from a fraction of the original oil boiling at 120—170°, boiled at 193—236°, and contained C, 61·3 ; H, 10·1 (between $C_5H_{10}O_2$ and $C_6H_{12}O_2$ and nearer the latter). The oil also contains sulphur (0·29 and 0·23 per cent. in the fractions 130—140° and 170—180° respectively), probably in the form of thiophen derivatives. C. F. B.

Bivalent Carbon: Chemistry of Methylene. By JOHN U. NEF (*Annalen*, 1897, **298**, 202—374. Compare Abstr., 1896, i, 71).—The theoretical portion of this paper is divided into six chapters, dealing with (1) the behaviour of unsaturated compounds, (2) the dissociation of saturated into unsaturated compounds, (3) the polymerisation of unsaturated compounds, (4) the condensation law, (5) the dissociation of condensation products into their original constituents, and (6) the methylene problem.

The author recognises two classes of unsaturated substances, namely,

(A) those which contain a double or treble linking between two neighbouring atoms, as, for example, ethylene, chlorine, acetylene, oxygen, the aldehydes, ketones and fatty acids, the alkylic cyanides, R·C⋮N, the nitroparaffins, O:NR:O, nitric acid, O:N(OH):O, sulphuric acid, $O:S(OH)_2:O$, the alkylic cyanates, and the thiocyanates ; and (B) those which contain an unsaturated atom, an atom, that is, which does not display its maximum valency, this class being typified by ammonia and the amines, methylene and its products of substitution, such as C:O, C:N·R, C:N·OH, thio-ethers, SR_2, alkylic chlorides, and imidogen, :NH. The process of saturation is not essentially different in the two classes, involving dissociation of the substances with which unsaturated compounds form additive products ; the substances (C) which undergo dissociation in this way are acids, ammonia derivatives, derivatives of water and of hydrogen sulphide, halogens, hydrogen, acidic chlorides, alkylic haloids, and halogen derivatives of metals and non-metals. Members of a further group of compounds (D) are frequently dissociated with even greater readiness than those last enumerated ; such are hydrocarbons, olefines, acetylene, and alkylacetylenes, compounds containing carbonyl, nitriles, nitro-compounds, methylpyridines, and methylquinolines, benzene, and the products of its substitution. It is represented that dissociation of a compound in this sense resolves it into hydrogen or halogen, and the residual complex.

The factors which determine the existence of an unsaturated substance are very numerous, and in some cases obscure, but the character and mass of radicles contained in a compound have great influence on its stability ; saturation is assisted in many cases by light, heat, electrical influences, and also by the action of acids, alkalis, water, and finely divided metals. The author considers it unnecessary to regard these agencies as catalytic, attributing their influence to mechanical causes ; they probably exert a dissociating influence on members of the foregoing classes, converting their components into the nascent state, in which condition they enter into combination, or undergo polymerisation. It is noteworthy that a polymeride is frequently resolved into the compound from which it is formed by the very agency which gives rise to its production.

Cases in which addition has been followed by spontaneous decomposition of the additive product have occurred with great persistence during the last few years, and the circumstance throws considerable doubt on the validity of the substitution hypothesis. It is conceivable that the process usually called substitution, in reality consists of dissociation of the radicles in which substitution is regarded as occurring, followed by addition to the substituent, the additive product being sufficiently unstable to lose spontaneously halogen hydride or water, as the case may be. The compounds which readily undergo this form of dissociation, or, in common language, the compounds which readily undergo substitution, are those comprised in class D. The readiness with which dissociation into hydrogen and hydrocarbon occurs, followed by addition to an unsaturated substance, is particularly influenced by the presence of negative radicles and atoms, and by the existence of double or treble linkings ; it is also increased by those agencies, such

as light and heat, which have been already recognised as exerting a favourable influence on dissociation, polymerisation, and addition phenomena.

It is necessary to distinguish clearly between polymerisation and condensation. Polymerised products are those which arise from the combination of free valencies in the same substance, such as benzene from acetylene; condensed products, on the other hand, are formed by the addition of members of class D to the unsaturated substances of A and B. It is possible to divide the majority of the condensation processes to which carbon compounds are liable into (1) ethylene condensation, (2) carbonyl condensation, and (3) methylene condensation. The first of these groups comprises the reactions of ethylic malonate, benzylic cyanide, deoxybenzoin, ethylic cyanacetate, and malononitrile, with alkylic haloids in which the alkylic radicle is ethyl or a higher homologue; the condensation of acetaldehyde to aldol, and of ethylic acetate to ethylic sodioacetoacetate also belong to this group, which includes the Friedel-Crafts reaction of hydrocarbons with aluminium chloride and alkylic haloid in which the alkylic group is ethyl or a higher homologue. The second division embraces all condensations of benzaldehyde, in acid solution, with phenols, tertiary aromatic amines, and ethylic malonate, the production of ethylic benzoylacetate from ethylic benzoate, sodium ethoxide, and ethylic acetate, and the condensation of ethylic oxalate with ethylic acetate, acetone, acetaldehyde, and benzylic cyanide; also the condensation of acidic chlorides with benzene, of phthalic anhydride with benzene, ethylic malonate, benzylic cyanide, quinaldine, and phenol, and of carbonic anhydride with phenols and the salts of substituted acetylenes. The third group includes the production of cinnamic acid from benzaldehyde, acetic anhydride, and sodium acetate, the condensation of benzaldehyde with ketones, aldehydes, and ethereal salts under the influence of sodium ethoxide or dilute caustic soda, the condensation of ethylic formate with ethylic acetate, acetone, and acetophenone, the conversion of formaldehyde into α-acrose and β-acrose, the condensation of benzylic alcohol, benzhydrol, and aromatic hydrocarbons under the influence of concentrated sulphuric acid, and the Friedel-Crafts reaction when carried out with methylic chloride.

The behaviour of benzene towards nitric and sulphuric acids is regarded by the author as the result of the addition of the dissociated hydrocarbon to the unsaturated molecule of the acid, followed by elimination of water from the product; similarly, the conversion of the hydrocarbon into bromobenzene is traced to the addition of the dissociated molecule to the unsaturated bromine molecule, Br⁝Br, when the additive compound, $HBr\dot{:}BrC_6H_5$, is produced, and spontaneously yields hydrogen bromide and bromobenzene.

It is pointed out that the same agents which induce condensation are instrumental in dissociating the product into its constituents. Ethylic acetoacetate, for instance, is resolved by sodium ethoxide into ethylic acetate, whilst mesitylic oxide, phorone, and ethylic ethylidenemalonate yield acetone, acetaldehyde, or ethylic malonate when heated with water or acids.

An investigation of numerous well-known derivatives of acetylene

has shown the author that these must be divided into two classes, (1) those derived from acetylene, CH:CH, usually characterised by agreeable odour and no marked chemical activity, and (2) derivatives of *acetylidene*, CH_2:C, which are poisonous, have an intensely disagreeable odour, are in some cases spontaneously inflammable, and generally exhibit great chemical activity. Behrend's di-iodacetylene, Sabanéeff's monobromacetylene, and Wallach's monochloracetylene are regarded as members of the latter class, and are referred to as *di-iodacetylidene*, *monobromacetylidene*, and *monochloracetylidene*, respectively. It is probable, also, that the metallic derivatives of acetylene belong to this group.

The experimental part of the paper comprises three divisions, which deal respectively with (I) reactions of nascent diphenylmethylene and phenylmethylene, (II) reactions of benzaldehyde, nascent hydroxyphenylmethylene and acetoxyphenylmethylene, and (III) the chemistry of acetylidene.

I.—According to Friedel and Balsohn, diphenylmethylic bromide yields benzhydrol and benzhydrol ether when heated with water. The author finds, however, that treatment with cold water during two weeks completely resolves diphenylmethylic bromide into hydrogen bromide and benzhydrol, whilst benzhydrol ether is formed on heating the bromide with 5 parts of water for 2 days on the water bath, if the hydrobromic acid is neutralised with alkali. It has been represented by Zincke and Thörner that benzhydrol ether has the constitution expressed by the formula $\begin{matrix}CPh_2\\ | \\ CPh_2\end{matrix}\!\!>\!O$, because it is produced when benzhydrol is heated at its boiling point for some time; from the following facts, however, it is necessary to regard the substance as a true ether of the formula $(CHPh_2)_2O$. Benzhydrol ether yields benzhydrol acetate (2 mols.) when treated with a mixture of cold glacial acetic (9 parts) and concentrated sulphuric (2 parts) acids: alcohol (10 parts) and concentrated sulphuric acid (2 parts) convert it, when gently heated, into benzhydrol ethyl ether: the solution in benzene is converted by concentrated sulphuric acid or by phosphoric anhydride into triphenylmethane. Moreover, the two expressions differ from one another by two atoms of hydrogen, and it has been shown by Klinger and Lonnes (Abstr., 1896, i, 687) that benzhydrol ether has the empirical formula $C_{26}H_{22}O$.

When benzhydrol ether is distilled rapidly under atmospheric pressure, it undergoes dissociation into diphenylmethylene and water, which associate in part on cooling; slow distillation gives rise to benzophenone and diphenylmethane, a small quantity of benzhydrol ether being found in the distillate. This observation is not in agreement with Linnemann's statement. Benzhydrol ether, however, boils at 267° under a pressure of 15 mm., without decomposing.

On heating benzhydrol or benzhydrol ether in a distillation flask, either alone or in an atmosphere of carbonic anhydride, water is eliminated, and after 3—5 hours, the products consist principally of benzophenone and tetraphenylethane, along with a small proportion of diphenylmethane. The changes involved are regarded by the author as taking place on the following lines. Benzhydrol is first dissociated into diphenylmethylene and water, just as formic acid yields carbon monoxide and water when heated at 167°; the methylene derivative

then unites with the benzhydrol which is in excess, yielding benzhydrol ether. The latter slowly dissociates at 300° into diphenylmethylene (2 mols.) and water, which reunite to form benzophenone, with liberation of hydrogen; the decomposition of water by nascent diphenylmethylene, $:CPh_2$, is attributed to the great affinity for oxygen which bivalent carbon exhibits. If water is in part removed from the sphere of action, diphenylmethylene undergoes polymerisation, yielding tetraphenylethylene, which is reduced by the nascent hydrogen; but if water is not removed, no trace of tetraphenylethane is produced, and the benzhydrol ether undergoes reduction, yielding diphenylmethane.

The same intermediate product, diphenylmethylene, is formed when benzilic acid is dissociated at 180—200°; as in the foregoing case, it decomposes the water which is present, yielding benzophenone, whilst the hydrogen thus liberated reduces unchanged benzilic acid to diphenylacetic acid (compare Klinger and Standke, Abstr., 1889, 885). To the production of diphenylmethylene may also be attributed the formation of tetraphenylethylene and tetraphenylethane when benzhydrol acetate and benhydrol benzoate are heated at 300°.

The uniform production of resinous polymerides which attends the treatment of benzylic derivatives with such agents as zinc dust or concentrated sulphuric acid, is attributed to the intermediate liberation of phenylmethylene, which then undergoes polymerisation. Thus zinc dust eliminates halogen hydride from benzylic bromide and benzylic chloride at 120°, the copper-zinc couple producing this effect on the former substance at ordinary temperatures, and in each case a dark-yellow resin of the formula $(C_7H_6)_n$ is produced; if, however, the halogen derivative is dissolved in an indifferent medium, the action is much milder, and the products are toluene and dibenzyl. This difference in behaviour is regarded as being due to the fact that, in the first case, a large proportion of phenylmethylene molecules are set free simultaneously, and then undergo polymerisation to complex molecules; on the other hand, dilution with an indifferent medium renders the dissociation much more gradual, and gives rise to polymerides of much smaller molecular weight.

The same observations apply to derivatives of benzhydrol and benzylic alcohol. Benzhydrol, benzhydrol ether, benzhydrol ethyl ether, benzhydrol acetate, and benzhydrol benzoate are all converted into red polymerides of diphenylmethylene under the influence of aluminium chloride, phosphoric anhydride, and concentrated sulphuric acid. The effect of introducing a diluent which is not an indifferent substance is similar to that produced in the Friedel-Crafts reaction, which meets with explanation on the dissociation basis developed in the paper. For instance, triphenylmethane is produced from a mixture of benzhydrol and benzene under the influence of phosphoric anhydride or concentrated sulphuric acid, and the hydrocarbon is also obtained from a solution of benzhydrol ether or benzhydrol acetate in benzene.

Friedel and Balsohn have observed that, whilst alcoholic ammonia converts diphenylmethylic bromide into benzhydrol ethyl ether, the aqueous base gives rise to benzhydrylamine, $CHPh_2 \cdot NH_2$, and dibenzhydrylamine, $NH(CHPh_2)_2$. This is explained on the assumption that diphenylmethylene takes up alcohol more readily than ammonia,

and ammonia more readily than water, and it is pointed out that the preference of unsaturated compounds for alcohol before water has been already exhibited in the cases of ethylic cyanimidocarbonate (Abstr., 1896, i, 72), cyanogen chloride, and cyanogen bromide. Although benzylic chloride yields benzyl ethyl ether under the influence of alcoholic potash, orthonitro- and paranitro-benzylic chlorides give rise to the corresponding stilbene derivatives in quantitative amount; similarly, chlorobenzylic cyanide and bromobenzylic cyanide are converted into dicyanostilbene. The behaviour of ethylic bromocyanacetate is, however, more remarkable.

Ethylic bromocyanacetate, CN·CHBr·COOEt, obtained by treating ethylic cyanacetate with bromine (1 mol.) at 150°, boils at 116° under a pressure of 25 mm. When dissolved in ether, and treated with metallic sodium, ethylic sodioacetoacetate, ethylic sodiocyanacetate, or aniline, it is converted exclusively into *ethylic dicyanofumarate*, COOEt·C(CN)⁚C(CN)·COOEt, which crystallises from benzene or alcohol in colourless needles, and melts at 122°. The substances enumerated may be regarded as dissociating ethylic bromocyanacetate into hydrogen bromide and ethylic cyanomethylenecarboxylate, COOEt·C(CN)⁚, which then undergoes polymerisation.

Ethylic bromomalonate, on the other hand, yields exclusively ethylic ethanetetracarboxylate, $(COOEt)_2CH{\cdot}CH(COOEt)_2$, when treated with ethylic sodiomalonate in absolute ether, no trace of the ethylenetetracarboxylate, $(COOEt)_2C{:}C(COOEt)_2$, being produced. This may be due to the initial dissociation of ethylic bromomalonate into hydrogen bromide and the methylenic derivative, $:C(COOEt)_2$, which then unites with ethylic malonate, set free from the sodium derivative by the halogen hydride. The behaviour of ethylic malonate towards unsaturated compounds gives some support to this view; for instance, Claisen has shown that ethylic ethylidenemalonate yields ethylic ethylidenedimalonate when heated with ethylic malonate at 200°, and by the action of benzylic cyanide on phthalic anhydride, Gabriel obtained the compound, $C_6H_4<\begin{matrix}CO\text{———}\\C(CPh{\cdot}CN)\end{matrix}>O$.

The foregoing facts have led the author to modify the views which have been previously expressed regarding the action of alkylic haloids on such compounds as ethylic sodiomalonate (Abstr., 1892, 140; 1893, i, 628). Instead of assuming that halogen hydride is first liberated, and that no direct displacement of sodium takes place (*loc. cit.*), the following explanation is put forward. When ethylic malonate is converted into ethylic methylmalonate by the action of methylic iodide on ethylic sodiomalonate, the alkylic iodide undergoes dissociation into methylene and hydrogen iodide, the latter removing the metal from ethylic sodiomalonate; the ethylic malonate which is thus liberated is then free to take up methylene, yielding ethylic methylmalonate. Support is lent to this view by the fact that ethylic ethylmalonate is readily produced from ethylic malonate and ethylic iodide and zinc, which also induces the introduction of two ethylic groups; it is more probable that the metal dissociates ethylic iodide into hydrogen iodide and ethylene, which is then absorbed by the ethereal salt, than that a zinc derivative of ethylic malonate is formed as an intermediate product. It is noteworthy that, whilst treatment of ethylic malonate with ethylic

iodide (1 mol.) and sodium ethoxide gives rise to a mixture of ethylic ethylmalonate and ethylic diethylmalonate in which the former preponderates, and ethylic ethylcyanacetate is produced in greater quantity than ethylic diethylcyanacetate when sodium ethoxide and ethylic iodide (1 mol.) act on ethylic cyanacetate, treatment of the last-named substance, on the other hand, with benzylic chloride (1 mol.) and sodium ethoxide yields more ethylic dibenzylcyanacetate than ethylic benzylcyanacetate. The author explains this phenomenon by attributing to ethylic malonate a greater capacity for dissociation than that exhibited by ethylic ethylmalonate, whilst ethylic benzylcyanacetate is regarded as undergoing dissociation with greater readiness than ethylic cyanacetate. On these lines, it is possible to account for the fact that ethylic ethylmalonate does not condense with acetaldehyde and benzaldehyde, differing in this respect from ethylic malonate.

It is probable also that the behaviour of benzylic cyanide and of deoxybenzoin towards alkylic haloids in presence of sodium ethoxide depends on the dissociation of the haloid into halogen hydride and alkylene, which is then absorbed by the benzylic cyanide and deoxybenzoin respectively. The same principle may be applied to the reactions of benzylic cyanide, ethylic malonate, ethylic cyanacetate, deoxybenzoin, and primary and secondary nitroparaffins, with nitrous acid, amylic nitrite, and phenyldiazonium chloride. The production of amines from ammonia and alkylic haloids may be also brought into this category.

Reverting to the action of metals on alkylic haloids, which has been investigated by Frankland, Würtz, and Fittig, the author points out that his hypothesis gains support from the fact that, in most cases, the product consists of a mixture of hydrocarbons. For instance, when sodium acts on methylic iodide in ether at 100°, methane, ethane, and ethylene are produced. This is readily explained on the assumption that methylic iodide is first dissociated into methylene and hydrogen iodide, which yields nascent hydrogen by the action of the metal, in quantity insufficient to convert the methylene entirely into methane; a part, therefore, becomes partly hydrogenised to methyl, which polymerises, a small proportion, however, escaping reduction and undergoing polymerisation, yields ethylene. As regards the mechanism of Fittig's synthesis of benzene homologues, it is maintained that when a halogen derivative of benzene is treated with methylic iodide and sodium, the benzene compound dissociates into hexacarbon tetrahydride, C_6H_4, and halogen hydride, whilst the methylic iodide yields methylene and halogen hydride. The metal liberates nascent hydrogen from the latter in quantity insufficient (in the absence of water) to reduce the unsaturated products further than phenyl and methyl respectively; they therefore unite, forming toluene.

II.—In an alcoholic solution of ethylenic dibromide, the latter may be regarded as existing in two conditions of dissociation, namely, ethylene and bromine, or vinylic bromide and hydrogen bromide; according as zinc dust or alkali is present, either of these conditions asserts itself. The author claims to have shown that ethylidene dihydroxide, $CHMe\cdot CH(OH)_2$, may undergo dissociation in three directions, represented by vinylic alcohol, $CH_2\colon CH\cdot OH$, acetaldehyde, $CHMe\colon O$, and hydroxyethylidene, $\colon CMe\cdot OH$; β-propylidene dihydr-

oxide, however, exhibits only two-fold dissociation into acetone and β-hydroxypropylene, $CH_2\colon CMe\cdot OH$, ω-dihydroxytoluene into $CHPh\colon O$ and $\colon CPh\cdot OH$, whilst orthacetic acid, $CMe(OH)_3$, is resolved into acetic acid, or dihydroxyethylene, $CH_2\colon C(OH)_2$. Chloral hydrate, however, undergoes four-fold dissociation, into (1) chloral and water, (2) hydroxytrichlorethylidene, $CCl_3\cdot C(OH)\colon$, (3) dichloracetylidene hydroxide, $CCl_2\colon C(OH)_2$, and hydrogen chloride, and (4) chloroform and dihydroxymethylene, $\colon C(OH)_2$.

Benzylidene diacetate, $CHPh(OAc)_2$, is prepared by heating benzaldehyde with equal weights of acetic anhydride and glacial acetic acid in a reflux apparatus at 150—180° for a short time, and submitting the product to distillation under a pressure of 20—30 mm.; it melts at 46°, and boils at 154° under a pressure of 20 mm. It is noteworthy that the compound is not produced by the action of acetic anhydride on benzaldehyde when the former is free from acetic acid; moreover, the anhydride prohibits the dissociation which benzylidene diacetate undergoes when exposed to the air during a prolonged period. A boiling solution of caustic soda acts very slowly on the substance, which is converted into cinnamic acid when heated with sodium acetate, either alone or in presence of glacial acetic acid; cold concentrated sulphuric or nitric acid resolves it into benzaldehyde and acetic acid.

The production of benzylidene diacetate is explained by assuming that benzaldehyde first forms with acetic acid the additive compound $OH\cdot CHPh\cdot OAc$, which dissociates into acetic acid and nascent benzaldehyde; the latter then dissociates acetic anhydride, producing benzylidene diacetate by addition.

Benzoic acetic peroxide, $AcO\cdot OBz$, is obtained by exposing a mixture of benzaldehyde and acetic anhydride (2 mols.) to the air until the liquid is free from aldehyde; in diffused light, this effect is produced in 43 days, exposure to sunlight for 20—25 days being generally sufficient. The oily product is agitated with 2—3 parts of cold concentrated nitric acid, which resolves benzoic acetic oxide into benzoic and acetic acids, and converts benzylidene diacetate into acetic acid and benzaldehyde; the liquid is then poured into water, extracted with ether, and the ethereal extract agitated with caustic soda, dried, and evaporated, the product being treated once more with concentrated nitric acid. It crystallises in colourless, transparent needles, and melts at 37—39°, exploding with considerable violence at 85—100°. It is possible to avoid the simultaneous production of benzoic acetic oxide by exposing benzaldehyde and acetic anhydride (1 part) mixed with sand (20 parts) to diffused daylight for 4 days in porcelain basins; the mass is extracted with ether, and the extract washed with sodium carbonate.

Benzoic acetic peroxide has a marked odour of ozone, decolorises a solution of indigo-sulphuric acid, and liberates iodine from potassium iodide. Cold dilute caustic soda slowly converts it into benzoic acid, sodium peroxide, oxygen, and benzoic peroxide, whilst sodium carbonate, although acting more slowly, gives rise to a greater proportion of benzoic peroxide; it sets free chlorine from concentrated hydrochloric acid, and is decomposed by concentrated sulphuric acid in an explosive manner. Its behaviour in general appears to indicate a tendency to dissociate into benzoic acetic oxide and ozone.

Metanitrobenzoic acetic peroxide, $AcO\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, is prepared by dissolving benzoic acetic peroxide in fuming nitric acid and pouring the liquid into water after an interval of 15 minutes; it crystallises from methylic alcohol in colourless needles, and melts at 68°.

Acetic peroxide $AcO\cdot OAc$, was first obtained by Brodie from barium peroxide and acetic anhydride, as an oil. It is more conveniently prepared by mixing hydrogen peroxide with acetic anhydride (2 mols.) at $-10°$, allowing the liquid to remain below 30° during 6 hours, diluting with ether, and then agitating with a 10 per cent. solution of sodium carbonate; the ethereal portion is dried and carefully evaporated, the residue being distilled with extreme caution under reduced pressure. Acetic peroxide forms transparent crystals and melts at 30°; it boils at 63° under a pressure of 21 mm., and explodes with great violence when heated above 100°, or on vigorous agitation. The odour is indistinguishable from that of ozone, and it probably owes its oxidising and explosive character to ready dissociability into that substance and acetic anhydride; if kept in loosely closed vessels, it is completely converted into acetic anhydride and acetic acid at the end of four months, and treatment with caustic soda rapidly yields acetic acid and sodium peroxide. Berthelot's ethylic peroxide, obtained by the action of ozone on ether, consists principally of acetic peroxide (compare also Vanino and Thiele, Abstr., 1896, i, 597).

Diphenylformal peroxide hydrate, $O_2(CHPh\cdot OH)_2$, is obtained by treating benzaldehyde (10 grams) with hydrogen peroxide (3 grams) in three portions, the temperature of the liquid being maintained below 30°; it melts at 60—62°, and is insoluble in cold ether and petroleum. Both in the solid state and when treated with sodium carbonate, it is dissociated into benzaldehyde and hydrogen peroxide without the formation of benzoic acid; cold acetic anhydride converts it into acetic peroxide, acetic acid, and benzaldehyde.

Ozone, acetic peroxide, and benzoic acetic peroxide have all the same odour, which is due either to atomic oxygen produced by their dissociation, or to the ozone formed from ordinary oxygen under the oxidising influence of atomic oxygen. The readiness with which the acidic derivatives of hydrogen peroxide dissociate into oxides and atomic oxygen suggests similar behaviour on the part of hydrogen peroxide itself, which would yield water and atomic oxygen; but it is well known that the substance dissociates also into nascent hydrogen and molecular oxygen, and this double dissociation affords an explanation of the simultaneously reducing and oxidising character of hydrogen peroxide. From this point of view, slow combustion in presence of water may be regarded as taking place in the following stages: (1) decomposition of water by the combustible material, (2) conversion of atmospheric oxygen into hydrogen peroxide by the nascent hydrogen produced, (3) dissociation of hydrogen peroxide into water and atomic oxygen, which then exerts direct oxidising action. Atmospheric oxygen never undergoes direct absorption.

Just as zinc, iron, lead, and phosphorus become oxidised at much lower temperatures in presence of caustic soda than when oxygen and water alone are present, so benzaldehyde, under the influence of caustic alkali, yields hydrogen, benzylic alcohol, and benzoic acid. This probably

depends on initial production of ω-dihydroxytoluene, which undergoes dissociation into phenylhydroxymethylene; the hydrogen liberated by the action of the latter substance on water reduces a portion of the aldehyde to benzylic alcohol, whilst the phenylhydroxymethylene takes up hydroxyl, the product becoming dissociated into benzoic acid and water. Similarly, formaldehyde yields methylic alcohol and formic acid. In this connection, the author emphasises the enormous importance of water in oxidation phenomena. The oxidation of aldehydes, ketonic alcohols, aldehydic alcohols, and members of the sugar group, depends, broadly speaking, on dissociation into a methylene derivative, which liberates nascent hydrogen from the water present; the nascent hydrogen then reduces the oxidising agent. In the same way is explained the production of formic and acetic acids along with alkali nitrite from nitroglycerol under the influence of alkalis, the formation of hydrogen along with formic and acetic acids on heating glycerol with solid potash, and the violently explosive character of nitroglycerol and methylic nitrate.

Amongst numerous cases with which the author illustrates his hypothesis is the phenomenon of fermentation. Organised ferments, or the enzymes which constitute their active principle, are regarded as capable of inducing dissociation of the sugar molecule; the methylene derivative thus produced decomposes water, setting free nascent hydrogen. Although, theoretically, a molecule of glucose is capable of dissociating in many different ways, a directive influence is exerted by the ferment, just as the dissociation of ethylenic dibromide is controlled by zinc dust or alkali.

Although phenylhydroxymethylene is capable of decomposing water and alcohol, these substances are not attacked if compounds are present which undergo dissociation more readily; such are acetaldehyde, acetone, acetophenone, ethylic acetate, benzylic cyanide, and ethylic malonate. It has been shown that benzylidene diacetate yields cinnamic acid when heated with sodium acetate at 180°, and it is on the intermediate formation of the first-named substance that the production of cinnamic acid from benzaldehyde, acetic anhydride, and sodium acetate depends. Benzylidene diacetate is dissociated by sodium acetate into phenylacetoxymethylene, to which acetic acid then adds itself; elimination of acetic acid from the product gives rise to cinnamic acid. It is shown experimentally that nascent benzaldehyde is not capable of adding acetic acid or the anhydride, and the synthesis in question is therefore ascribed to phenylacetoxymethylene; it cannot, however, be settled definitely whether it is acetic acid, sodium acetate or acetic anhydride which unites with the nascent phenylacetoxymethylene.

The conversion of benzaldehyde into benzoin is traced as follows. Alcohol with benzaldehyde forms the additive compound,

$$OH\cdot CHPh\cdot OEt,$$

which, under the influence of potassium cyanide, is dissociated into alcohol and phenylhydroxymethylene; the later polymerises to the ethylene derivative, $OH\cdot CPh\colon CPh\cdot OH$, to which alcohol is added and then eliminated from the product, yielding benzoin. The deleterious effect of sodium ethoxide is due to the fact that the additive compound

of benzoin and alcohol, OEt·CPh(OH)·CHPh·OH, yields benzaldehyde under the influence of that substance.

Benzaldehyde owes its conversion into hydrobenzamide, in the first place, to the production of the additive compound, $OH·CHPh·NH_2$; this undergoes dissociation into water and phenylamidomethylene, which polymerises to diamidostilbene, the latter becoming added to benzaldehyde, and yielding hydrobenzamide.

In the condensation of acetaldehyde to aldol by means of acids and alkalis, the author recognises vinylic alcohol as an intermediate product. An aqueous solution of acetaldehyde may be regarded as containing ethylidene dihydroxide, $CHMe(OH)_2$, which, on elimination of water, becomes dissociated into three products, acetaldehyde, hydroxyethylidene, and vinylic alcohol; the last-named substance then undergoes ethylene condensation with ethylidene dihydroxide, yielding aldol and water. The *basic mercury* derivative of vinylic alcohol, $(C_2H_3O)_2Hg,HgO$, is produced when an aqueous solution of acetaldehyde is added to freshly precipitated mercuric oxide, and agitated with sodium carbonate or caustic soda; it is a white powder which gradually decomposes in the desiccator, yielding acetaldehyde, which is immediately produced under the influence of dilute hydrochloric or sulphuric acid. The action of acetic and benzoic chlorides is very vigorous, and bromine converts it into substitution products of acetaldehyde.

The formation of ethylic acetoacetate, and of condensation products of acetone with acids and ammonia, must be also regarded as due to ethylene condensation. The ortho-compound,

$$COOEt·CH_2·C(OEt)_2·ONa,$$

obtained from ethylic malonate and sodium ethoxide, loses alcohol and yields the ethylene derivative, ethylic sodiomalonate,

$$COOEt·CH:C(OEt)·ONa$$

(compare Abstr., 1892, 140). Similarly, from ethylic acetate and sodium ethoxide, arises the ethylene derivative, $CH_2:C(OEt)·ONa$, which is incapable of free existence, and therefore unites with ethylic acetate, acetone, or acetophenone, forming the sodium derivative of ethylic acetoacetate, acetylacetone, or benzoylacetone respectively.

It has been now for many years generally accepted that the production of ether from alcohol and concentrated sulphuric acid at 140° depends on the initial production of ethyl hydrogen sulphate, which undergoes double decomposition with a second molecule of alcohol, yielding ether and sulphuric acid. The author, however, prefers to regard the change as involving dissociation of ethyl hydrogen sulphate into sulphuric acid and nascent ethylene, which is then absorbed by the alcohol present; the production of ether from ethylic iodide and sodium ethoxide is explained on similar lines. The presence of nascent ethylene harmonises with the formation of large quantities of ethylic chloride when ethylic alcohol is treated with sulphuric acid and sodium chloride, although very little is produced when alcohol is heated with hydrogen chloride; moreover, whilst it is possible to actually separate methylic alcohol and concentrated nitric acid by distillation, the presence of concentrated sulphuric acid at once gives rise to methylic nitrate, owing to the dissociation of the methyl hydrogen sulphate into methylene, which then unites with nitric acid.

The slow combustion of dry ether to acetaldehyde, acetic acid, and hydrogen peroxide, the production of ethylic peroxide under the influence of ozone, and the recognition of divinyl ether as a product of spontaneous decomposition, now meet with analogous explanation. With regard to divinyl ether, which was supposed by Poleck and Thümmel to be vinylic alcohol (Abstr., 1890, 118), it must be mentioned that its identity is not fully established; as, however, a solution of mercuric chloride in hydrogen potassium carbonate yields no precipitate, it cannot be vinylic alcohol. The production of formaldehyde and formic acid along with hydrogen peroxide, acetaldehyde, and acetic acid (Legler, Abstr., 1886, 327), when the combustion of ether is effected at 260—500°, depends on the formation of ethylene, which is dissociated into methylene; the latter burns to hydrogen peroxide and dihydroxymethylene, which further oxidation converts into orthoformic acid. The compound, $(C_2H_6O_4)_3$, obtained by Legler, arises from formaldehyde and hydrogen peroxide, and is therefore regarded as formal peroxide hydrate, $O_2(CH_2{\cdot}OH)_2$. The exclusive production of formaldehyde when ethylene is burnt in oxygen at 400° is also explained on the assumption that the hydrocarbon is dissociated into methylene.

In this connection, the author describes an attempt to produce free methylene. Methylenic iodide is slowly converted into formaldehyde when heated with mercury in air at 100°, and the same product is formed on heating the methylene additive compounds, CH_2,HgI_2 and CH_2,Hg_2I_2, in air. If, however, the operation is carried out in an atmosphere of nitrogen at 180°, ethylene is the sole product. Methylene is probably liberated, and, in the absence of an oxidising agent, undergoes polymerisation.

It is well known that the slow oxidation of animal and vegetable matter, and many carbon compounds, is associated with the production of hydrogen peroxide and active oxygen, and is also accompanied by phosphorescence phenomena (Radziszewski, Abstr., 1881, 488). It has been already pointed out that the two-fold dissociation of hydrogen peroxide can give rise to both atomic oxygen and hydrogen, and the author maintains that the phosphorescence phenomena are due to the formation of methylene by dissociation of the organic matter, the hydrocarbon undergoing combustion in moist air in a manner resembling the ignition of phosphorus and other spontaneously inflammable substances.

III.—Tetrabromethylene, $CBr_2{:}CBr_2$, is obtained by adding bromine (3 mols.) to silver acetylide suspended in water, the liquid being continuously agitated meanwhile; it melts at 56°, and boils at 100°, 104°, and 109°, under pressures of 15 mm., 20 mm., and 25 mm., respectively.

Asymmetric dibromovinyl ether, $CBr_2{:}CH{\cdot}OEt$, is prepared by heating tetrabromethylene with alcohol in which sodium (4 mols.) has been dissolved; the product may be separated into two fractions, the portion boiling at 72—73° under a pressure of 33 mm. consisting of ethylic bromacetate and dibromovinyl ether. On treating the mixture with ammonia, ethylic bromacetate is converted into bromacetamide, leaving dibromovinyl ether undissolved; the latter boils at 75—76°,

under a pressure of 30 mm. Concentrated nitric acid converts dibromovinyl ether into ethylic dibromacetate. Cold alcoholic sodium ethoxide (1 mol.) gives rise to ethylic bromacetate, but ethylic ethoxyacetate is produced with excess of the agent.

Asymmetric dibromovinyl ether is identical with the dibromovinyl ether obtained by Sabanéeff from acetylene dibromide and alcoholic potash; its production from tetrabromethylene is explained by assuming its dissociation into bromine and dibromacetylidene, $CBr_2\colon C$, which takes up alcohol. Acetylene dibromide, on the other hand, is dissociated in two directions, (1) into hydrogen bromide and bromacetylidene, $CHBr\colon C$, and (2) into acetylene and free bromine, which immediately unites with bromacetylidene, forming tribromethylene, $CHBr\colon CBr_2$; the latter is dissociated by alkali into hydrogen bromide and dibromacetylidene, which takes up alcohol, yielding dibromovinyl ether.

Di-iodacetylidene, $CI_2\colon C$, prepared by treating tetriodethylene with alcoholic sodium ethoxide (2 mols.), crystallises from petroleum in needles melting at 81°; it is also produced by the action of sunlight on tetriodethylene, and by the action of iodine on silver acetylide suspended in ether. The substance has been hitherto regarded as di-iodacetylene, $CI\colon CI$, and is also formed when alcoholic potash acts on acetylene di-iodide, $CHI\colon CHI$, acetylene being liberated; this change is analogous to the conversion of acetylene dibromide into acetylene and dibromovinyl ether. Di-iodacetylidene is very volatile, and has the odour of phenylic isocyanide, its vapour attacking the eyes; it is readily soluble in all organic solvents excepting petroleum. Slow oxidation in neutral solution converts it into carbonic oxide and tetriodethylene (compare Biltz, Abstr., 1897, i, 390), but the process is completely checked by the addition of caustic alkali.

Tri-iodovinylic nitrate, $CI_2\colon CI\cdot O\cdot NO_2$, is obtained on dissolving di-iodacetylidene in cold, fuming nitric acid, which liberates carbonic anhydride and iodine; it crystallises from a mixture of benzene and petroleum in yellow needles, and melts at 109—110°.

When di-iodacetylidene is heated alone at 80—100°, it explodes violently, yielding iodine and carbon, but the solution in alcohol, glacial acetic acid, or petroleum, is not completely decomposed when heated with finely divided metals at 100° for 12 hours, although it gives rise to tetriodethylene. Acetylene is formed when di-iodacetylidene is reduced with sodium amalgam or sulphuric acid and zinc dust, and the hydrocarbon is also produced in small quantity along with carbonic oxide when the substance is treated with alcoholic sodium ethoxide at 100°; excess of the latter agent gives rise to a mixture of ethylic iodacetate and *ethylic orthiodacetate*, $CH_2I\cdot C(OEt)_3$, which is a colourless, pungent oil, and boils at 93° under a pressure of 14 mm.

Asymmetric dibromodi-iodethylene, $CI_2\colon CBr_2$, is prepared by adding bromine (1 mol.) dissolved in chloroform to a solution of di-iodacetylidene in the same medium; it crystallises from glacial acetic acid in yellowish leaflets, and melts at 95°. Alcoholic sodium ethoxide eliminates bromine from the compound, yielding di-iodacetylidene.

Bromacetylidene, $CHBr\colon C$, is identical with bromacetylene, prepared

by Sabanéeff from acetylene dibromide, by treating it with alcoholic soda. It boils at $-2°$, and burns spontaneously in air, yielding hydrogen bromide, carbon, carbon monoxide, and carbonic anhydride; in a very limited atmosphere, combustion is slow, and acetylene dibromide is produced. The vapour is poisonous, and has the odour of phosphorus vapour; moreover, its solutions in dilute nitric acid, water, or alcohol, which have the odour of ozone, exhibit phosphorescence during many days, and give ozone reactions. Although bromacetylidene acts vigorously with halogens and halogen hydrides, it is indifferent towards ethylic hypochlorite.

Bromacetylidene di-iodide (*di-iodacetylidene hydrobromide*, or *asymmetric di-iodobromethylene*), $CHBr:CI_2$, is obtained by passing bromacetylidene into an ethereal solution of iodine; it boils at 104° under a pressure of 10 mm. Alcoholic sodium ethoxide, or potash, converts it into di-iodacetylidene, which is also produced under the influence of alcoholic sodium phenoxide and alcoholic potassium acetate (at 100°); in this respect, it resembles ethylic bromocyanacetate, from which hydrogen bromide is eliminated under similar conditions. Di-iodacetylidene hydrobromide, however, undergoes no change when heated with sodium acetate and a small quantity of glacial acetic acid at 150° during 12 hours, and it is also indifferent towards silver acetate at 100°.

Tri-iodobromethylene, $CI_2\cdot CBrI$, is a bye-product in the preparation of the foregoing substance, and remains as a crystalline residue in the distilling flask; it crystallises from glacial acetic acid in yellowish leaflets, and melts at 135°. Alcoholic sodium ethoxide, or potash, converts it into di-iodacetylidene, which is also produced under the influence of sunlight.

The paper concludes with a discussion of the general behaviour of trihaloid and tetrahaloid derivatives of methane, and of certain phases of molecular rearrangement, on the lines already laid down.

M. O. F.

Action of Sulphuric Acid on Coal Gas. By P. FRITZSCHE (*J. pr. Chem.*, 1897, **56**, 258—265).—Berthelot (this Journal, 1876, ii, 183) has shown that when coal gas is passed through concentrated sulphuric acid, brown coloured substances are formed consisting of condensation products of substituted acetylenes. The author now shows that the nature of the products varies with the coal gas examined and in no case is the formation of these substances so simple as Berthelot's experiment suggested.

Coal gas freed from benzene and hydrogen sulphide was treated with concentrated sulphuric acid in iron vessels under a pressure of about 4 atmospheres. From the oily product thus obtained crystals separated on cooling, which proved to be the iron salt of a sulphonic acid. By treating all the oil with caustic soda, considerable amounts of the sodium salt of the same acid were obtained, and from this the *copper*, *sodium*, *ammonium*, *iron*, and *calcium* salts were prepared.

The *free acid*, liberated from the copper salt by treatment with hydrogen sulphide, forms white crystals readily soluble in water, is very stable, not being acted on by hot concentrated sulphuric acid,

and appears to be the sulphonic acid of a substance having the formula $C_{15}H_{26}O$. This may probably be cedar camphor, a supposition supported by the fact that camphors, as a rule, form stable sulphonic acids.

At least one other substance of similar constitution exists in the mother liquor from the sodium salt, and will be further investigated.

A. W. C.

Preparation of Bromonitromethane. By JOSEPH TCHERNIAC (*Ber.*, 1897, **30**, 2588).—Bromonitromethane can readily be prepared by dissolving 15 grams of nitromethane in baryta water, cooling with ice and adding the solution to 39 grams of bromine covered with pieces of ice; the excess of bromine is then removed by sulphurous acid and the liquid distilled, when 18 grams of the pure compound is obtained.

A. H.

Acetylene Di-iodide. By GUILLAUME L. J. DE CHALMOT (*Amer. Chem. J.*, 1897, **19**, 877—878).—In reference to the preparation of this substance by Biltz (Abstr., 1897, i, 389), the author states that he obtained it some years ago in preparing ethylene tetriodide by Maquenne's method, using calcium carbide instead of barium carbide. The alcoholic washings of the crude tetriodide were diluted with water, when acetylene di-iodide was precipitated together with some oily matter. It crystallised from alcohol or ether in long, transparent needles and melted at 82°. By adding iodine to a solution of acetylene in potassium hydroxide solution, no ethylene tetriodide was formed, but a white precipitate was produced which crystallised from benzene in needles; it has a very pungent odour and attacks the mucous membrane especially of the eyes. A similar compound prepared with bromine is an oil which takes fire spontaneously on exposure to the air and has a very disagreeable odour.

E. W. W.

Regularities in the Boiling-points of Isomeric Aliphatic Compounds. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1897, **30**, 2784—2791).—When the boiling points of the various amylic and hexylic alcohols are compared amongst each other, the same regularities are observed as with the constant of velocity of reaction (this vol., i, 119), the normal compounds having the higher boiling point, which is lowered by the introduction of side chains, according to their position, size, and number, in the manner already described. The alcohols are peculiarly favourable for such a comparison, because the greatest difference of boiling point exhibited by a set of isomerides is larger than in the case of other compounds, and, moreover, increases with the number of carbon atoms present. But similar regularities can be observed with other compounds of the type $X\cdot[CH_2]_n\cdot CH_3$ and their isomerides, where $X = I$, $CH_3\cdot COO$, NH_2, or COOH; and also with compounds of the type $X\cdot[CH_2]_n\cdot X$ and their isomerides, where $X = Br$, OH, or CH_3.

C. F. B.

2:4-Hexadi-inediol-1:6. By ROBERT LESPIEAU (*Compt. rend.*, 1896, **123**, 1295—1296).—$OH\cdot CH_2\cdot C⋮C\cdot C⋮C\cdot CH_2\cdot OH$, is obtained when the copper derivative of propargylic alcohol is oxidised with potassium ferricyanide and the product treated with ether. It is a colourless, crystalline solid melting at 111—112° and turning

yellow or rose-coloured under the action of heat or light. It dissolves in water, alcohol, ether, and acetic acid. The most suitable agent for purification is boiling benzene, from which it crystallises on cooling. At $-15°$, it combines with 4 atoms of bromine. Its glycolic nature was proved by converting it into the diacetin. The *dimethylic ether*, $OMe\cdot CH_2\cdot C⋮C\cdot C⋮C\cdot CH_2\cdot OMe$, is obtained when methyl propargyl ether is oxidised. It is a colourless liquid which turns brownish-red on exposure to light; it melts at $-9°$, distils at 104·5—105·5° under a pressure of 12—13 mm., has the sp. gr. $= 0·9969$, and at $-15°$ combines with 4 atoms of bromine. J. J. S.

New Synthesis of Glycerol and of Dihydroxyacetone. By OSCAR PILOTY (*Ber.*, 1897, **30**, 3161—3169. Compare Abstr., 1897, i, 453).—When bromine acts on an aqueous solution of dihydroxyacetoxime (*loc. cit.*), nitrous oxide is eliminated, and dihydroxyacetone produced; reduction of the ketone with sodium amalgam converts it into glycerol, a step which completes the synthesis of that substance from formaldehyde. The different stages by which the synthesis is effected are the following. Nitromethane converts formaldehyde into teritary nitrotrihydroxybutane, $NO_2\cdot C(CH_2\cdot OH)_3$, which on reduction yields hydroxylaminotrihydroxybutane, $OH\cdot NH\cdot C(CH_2\cdot OH)_3$; oxidation with mercuric oxide eliminates formaldehyde from this substance, giving rise to dihydroxyacetoxime, $OH\cdot N⁚C(CH_2\cdot OH)_2$, which is then treated in the manner already indicated.

Dihydroxyacetone, $CO(CH_2\cdot OH)_2$, is prepared by adding bromine (15 grams) to a solution of dihydroxyacetoxime (10 grams) in water (100 c.c.), the temperature being allowed to rise to 40°; by a method of purification which is detailed in the original paper, the ketose is obtained as a white solid, which crystallises from much boiling acetone in flat, prismatic plates melting at 68—75°. Dihydroxyacetone dissolves with extraordinary readiness in water, and tastes sweet, producing a cooling sensation on the tongue; it exerts vigorous reducing action on cold Fehling's solution, and when a 1 per cent. solution is boiled with the agent, the reduction effected is equal to that produced by an equal weight of grape sugar under the same conditions. The ketose, however, is not fermented by yeast. When the aqueous solution is treated with phenylhydrazine and acetic acid, the phenylosazone is produced, crystallising from benzene in elongated, prismatic leaflets melting at 132°; this compound was obtained by E. Fischer and Tafel (Abstr., 1888, 1264) from glycerose, and by Piloty and Ruff (Abstr., 1897, i, 454) from dihydroxyacetoxime. The *sodium hydrogen sulphite* compound crystallises from dilute alcohol in stellate groups of slender needles. Dihydroxyacetone is reduced to glycerol by means of sodium amalgam in an aqueous solution of aluminium sulphate.

If the syrup from which dihydroxyacetone is first separated remains for some time without being sown with a crystal of the substance, a *compound* separates in minute crystals, and when recrystallised from alcohol, melts at 155°; it has a sweet taste, reduces hot Fehling's solution, and appears to be identical with the substance obtained from dihydroxyacetone when an attempt is made to crystallise it from alcohol. Another *compound* is produced when the solution of di-

hydroxyacetone is evaporated in a vacuum at 65—70°; it is a white solid, resembling crude starch, and is insoluble in absolute alcohol. It dissolves very slowly in boiling water, and yields, with dilute acids, a turbid liquid which reduces cold, alkaline copper oxide. These two substances are doubtless polymerides or anhydrides of dihydroxyacetone.

The author discusses the part which is played by formaldehyde in the chemistry of vegetable physiology. M. O. F.

Reactions of Potassium Ferricyanide with Glucose and their Application to Volumetric Analysis. By N. TARUGI and G. NICCHIOTTI (*Gazzetta*, 1897, **27**, ii, 131—153).—The authors show that the reaction between potassium ferricyanide and glucose in boiling potash solution depends on the concentration; the reaction is represented in normal solutions by the equation $10K_3FeCy_6 + 17KHO + 2C_6H_{12}O_6 = 10K_4FeCy_6 + 2K_2CO_3 + 2C_2H_3O_2K + 12H_2O + C_6H_{11}O_7K$, in N/10 solutions by the equation $10K_3FeCy_6 + 21KHO + 4C_6H_{12}O_6 = 10K_4FeCy_6 + C_6H_{11}O_7K + 8C_2H_3O_2K + 2KHCO_3 + 46H_2O$, and in N/40 solutions by the equation $10K_3FeCy_6 + 19KHO + 5C_6H_{12}O_6 = 10K_4FeCy_6 + 5C_6H_{11}O_7K + 4KHO + 10H_2O$. The course of these reactions was followed by determinations of the velocity of reaction.

Working with solutions of either of these three concentrations, with potash, glucose, and potassium ferricyanide, if the concentrations of two of the solutions are known, that of the third can be determined. W. J. P.

Caroubinose and *d*-Mannose. By W. ALBERDA VAN EKENSTEIN (*Compt. rend.*, 1897, **125**, 719).—The caroubinose described by Effront (*Compt. rend.*, 1897, **125**, 309) is identical with the *d*-mannose described by the author (Abstr., 1896, i, 272). The higher rotatory power observed by Effront is probably due to the presence of products of incomplete saccharification, possibly a bihexose derived from two mannose groups. C. H. B.

Biological Production of Levulose from Mannitol. By CAMILLE VINCENT and BÉNÉDICT DELACHANAL (*Compt. rend.*, 1897, **125**, 716—717).—When the ferment of sorbose is cultivated in a mineralised peptone solution containing 3 per cent. of mannitol, the mannitol is oxidised and converted into levulose. This change is the converse of the production of mannitol from levulose by the action of sodium amalgam. C. H. B.

Humin Formation from Sugar on Oxidation with Potassium Permanganate. By H. VON FEILITZEN and BERNHARD TOLLENS (*Ber.*, 1897, **30**, 2581—2584).—The authors do not agree with Benni's conclusions, and find that the brown precipitate formed by the oxidation of sugar with potassium permanganate has nothing to do with humin substance, but consists for the most part of oxide of manganese and potassium hydroxide, and contains only 0·5—0·7 per cent. of carbon. J. F. T.

Hydrolysis of Starch by Diastase. By PAUL PETIT (*Compt. rend.*, 1897, **125**, 355—357).—Starch was hydrolysed at 70° with precipitated diastase (1 per cent.) until the colour with iodine no longer changed.

The red coloration thus obtained could only be destroyed by the addition of larger quantities of diastase.

The liquid which gave the red coloration was concentrated, and after cooling, fermented with yeast; after filtration and concentration a syrup was obtained, which was precipitated with alcohol, purified, washed and dried thoroughly. The last traces of sugar were removed by extracting with absolute alcohol in a Soxhlet tube for 8 hours. Dextrin D as thus obtained is a white, non-hygroscopic powder; its composition is probably $(C_6H_{10}O_5)_3$, its specific rotatory power $\alpha_D = +176 \cdot 4°$, and its reducing power $R = 14 \cdot 93$. It gives no osazone, and yields glucose when hydrolysed by boiling for about 3 hours with dilute hydrochloric acid; when boiled for a shorter time, a mixture of glucose with a biose is obtained, the osazone of the latter melting at 180—181°. The action of diastase on dextrin D has also been studied. J. J. S.

Aliphatic Carbon Chains. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1897, **30**, 2775—2784).—This paper gives the results of an investigation, the details of which have been published in *J. Russ. phys.-chem. Soc.*, **29**, 444. The velocity of reaction of primary amines with allylic bromide in fifteen times their weight of benzene and at 100° has been examined; the values of the constant of velocity $k = (A - \frac{1}{2}x)/(A - x)t$ are tabulated below. As regards nomenclature, the Greek letter indicates the position of the side chain (which, with but one exception, is methyl); thus $NH_2 \cdot CHMe \cdot CHMe \cdot CH_3$ is $\alpha\beta$-amylamine.

	Methyl-amine.	Ethyl-amine.	Propyl-amines.	Butyl-amines.	Amyl-amines.	Hexyl-amine.
Normal	8302	3807	3783	3886	3790	3537
γ					2985	
β				2759		
α			1257	1240	1189	
[*α-ethyl*]					[672]	
$\alpha\beta$					586	
$\alpha\alpha$				314	270	

Inspection of the table shows that the formation of a carbon chain by the change from methylamine to ethylamine is attended by a marked diminution of the constant. Once a chain is formed, however, the elongation of this chain, so long as it remains primary, has but little effect on the constant, the normal primary aliphatic amines, with the exception of methylamine, having approximately the same constant. The introduction of a side chain lowers the constant, and the more so the nearer it is to the amido-group; in the one case of α-ethyl, as compared with α-methyl (amylamine), it is seen that the elongation of a side chain produces a further diminution of the velocity of reaction. The introduction of a second side chain further diminishes the velocity, and in the same manner as before, a minimum value of the constant being obtained when both side chains are in the α-position.

The old measurements of the rate of etherification of aliphatic alcohols show the same regularities, the hydroxyl group here replacing the amido-group of the amines. C. F. B.

Action of Hydrogen Sulphide and of Carbon Bisulphide on Trimethyltrimethylenetriamine. By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1896, [vii], 9, 119—133).—This work has been published previously in an abridged form (see Abstr., 1897, i, 456). J. J. S.

Derivatives of Prozan. By JOHANNES THIELE and WILHELM OSBORNE (*Ber.*, 1897, 30, 2867—2869).—By the action of potassium cyanide on diazoguanidine nitrate, there is obtained, beside much amidotetrazole, *diazoguanidine cyanide*, $N⋮C \cdot N⁚N \cdot NH \cdot C(NH_2)⁚NH$; this is a yellowish substance which decomposes above 200°; in it the CN group can be converted into $CO \cdot NH_2$, $C(NH_2)⁚NH$, $C(NH_2)⁚NOH$, COOEt, &c., by the usual methods. These are the first aliphatic diazo-amido-compounds that have been obtained.

Formamidodiazoamidoformamidine, $NH_2 \cdot CO \cdot N⁚N \cdot NH \cdot C(NH_2)⁚NH$, crystallises with $1H_2O$ in yellow needles which explode at 140°; the colourless *hydrochloride* explodes at 141°. *Ethylic formamidinediazo-amidoformate*, $COOEt \cdot N⁚N \cdot NH \cdot C(NH_2)⁚NH$, is yellow, and melts at 162°. Both of these substances unite with sulphurous acid in the cold, and the products, $NH_2 \cdot CO \cdot NH \cdot N(SO_3H) \cdot NH \cdot C(NH_2)⁚NH$ and $COOEt \cdot NH \cdot N(SO_3H) \cdot NH \cdot C(NH_2)⁚NH$, must be regarded as derivatives of prozan, $NH_2 \cdot NH \cdot NH_2$. It was not possible, however, to isolate prozan from them; unlike hydrazine, it seems to be very unstable. C. F. B.

Action of Sodium on Methyl Propyl Ketone and on Acetophenone. By PAUL C. FREER and ARTHUR LACHMANN (*Amer. Chem. J.*, 1897, 19, 878—890).—The action of sodium on a dilute solution of methyl propyl ketone in ether gives rise to a white, flocculent precipitate of the formula C_5H_9ONa, hydrogen being evolved; this substance is fairly stable in dry air, but is decomposed by water. As it is probably of a complex nature, like the analogous sodium acetone, the action of sodium suspended in ether on a mixture of the ketone with benzoic chloride was investigated; the product was treated with alkali, which dissolved a large quantity of benzoic acid, and a trace of an undetermined fatty acid.

Dibenzoylmethyl Propyl Ketone, $CHBz_2 \cdot COPr$ or $OH \cdot CPh⁚CBz \cdot COPr$.—This melts at 115°, is almost insoluble in cold alcohol and ether, and is best purified by dissolving it in boiling alcohol, from which it separates in white, amorphous flakes. It gives an intense red coloration with ferric chloride, is soluble in alkalis and alkali carbonates, and is slowly precipitated from such solutions by carbonic anhydride. By varying the strength of the alcohol from which it is crystallised, and the rate of cooling, the melting point of the product varies between 101° and 115°; in some cases, also, it gives only a very faint ferric chloride reaction. This may be due to the existence of two modifications analogous to that of Claisen's similarly constituted dibenzoylacetylmethane (*Annalen*, 291, 73). It is only very slowly hydrolysed by alkalis. It gives several products with phenylhydrazine, one of which forms long needles, and melts at 110°.

The original ethereal solution contains the benzoyl compounds of methyl propyl ketone and of methyl propyl carbinol, and the *iso*-ketone $CH_2:CPr\cdot OH$, seemingly in the form of its hydrogen chloride compounds. The action of benzoic chloride on sodium methyl propyl ketone would thus appear to be similar to its action on sodium acetone, and the sodium compound would have the constitution represented by the formula $ONa\cdot CPr^{\alpha}:CH_2$.

By the action of sodium on a mixture of benzoic chloride and acetophenone under conditions similar to those described in the previous reaction, the authors obtained di- and tri-benzoylmethane from the alkaline extract, whilst the ethereal solution, on fractionation under 14 mm. pressure, yields an oil containing acetophenone and chlorinated derivatives. The thick tarry residue, on saponification with potash, gives benzoic acid and tribenzolymethane, and with dilute sulphuric acid at 160°, benzoic acid, acetophenone-pinacone, and a ketone which boils at 180—182° under 14 mm. pressure. This ketone contains chlorine, gives a deep red coloration with ferric chloride, is insoluble in alkalis, and reacts with phenylhydrazine. The reaction is, therefore, similar to that with methyl propyl ketone, except that no isoketone benzoate is formed. Hence sodium acetophenone has a constitution represented by the formula $ONa\cdot CPh:CH_2$.

The action of sodium on mesityl oxide was also investigated, but no definite results were obtained.

Diethyl ketone in ethereal solution is attacked by sodium with liberation of hydrogen, forming a white sodium compound, which seems to be more stable than sodium acetone or sodium methyl propyl ketone, but resembles them in properties. E. W. W.

Action of Hydroxylamine on Phorone. By Carl D. Harries and Fritz Lehmann (*Ber.*, 1897, **30**, 2726—2737. Compare Abstr., 1897, i, 211).—It has been several times observed that unsaturated ketones differ considerably from saturated ones in their behaviour towards hydroxylamine. The authors, for instance, have shown that phorone gives rise to three substances, none of which is the normal oxime (*loc. cit.*), and three hydroxylamine derivatives have been also obtained from benzylideneacetophenone (Claus, Abstr., 1897, i, 189); Tiemann has found that isocamphorone yields hydroxylaminodihydrocamphorone-oxime under the influence of alcoholic hydroxylamine when the ketone is in excess (*loc. cit.*, i, 200), and Knoevenagel, generalising from the behaviour of ketones of the type $RCO\cdot CR:CHR$, has shown that they are converted into derivatives of the constitution $\begin{matrix} CHR\cdot CHR \\ | \qquad\qquad \\ CR = N \end{matrix}\!\!>\!O$ (compare Abstr., 1896, i, 189).

Returning to their study of the action of hydroxylamine on phorone, the authors find that treatment with a cold solution of the base in absolute alcohol gives rise to triacetonedihydroxylamine,

$$OH\cdot NH\cdot CMe_2\cdot CH_2\cdot CO\cdot CH_2\cdot CMe_2\cdot NH\cdot OH,$$

the anhydride, $CO<\begin{matrix}CH_2\cdot CMe_2\cdot NH\\CH_2\cdot CMe_2\cdot NH\end{matrix}>O$, being formed if the liquid is warmed with water and free alkali; triacetonehydroxylamine, $CO<\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}>NOH$, described in the previous paper (Abstr., 1897,

i, 212), is produced by the action of hydroxylamine (1 mol.) on phorone in presence only of free sodium ethoxide; this is analogous to the conversion of phorone into triacetoneamine, $CO<\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}>NH$, under the influence of ammonia.

Triacetonedihydroxylamine,

$$OH\cdot NH\cdot CMe_2\cdot CH_2\cdot CO\cdot CH_2\cdot CMe_2\cdot NH\cdot OH,$$

is obtained by adding a solution of free hydroxylamine (2 mols.) in 400 c.c. of methylic alcohol to 50 grams of phorone dissolved in 100 c.c. of the same medium; after 4 days, the liquid is diluted with ether (2 vols.), filtered, and treated with anhydrous oxalic acid (33 grams) dissolved in ether, the oxalate which is thus obtained being finally dissolved in dilute hydrochloric acid and mixed with potassium carbonate. The base is a colourless, syrupy liquid, which boils at 135° under a pressure of 20 mm., without undergoing decomposition if small quantities are manipulated; it dissolves readily in water, and is very soluble in alcohol, ether, light petroleum, and benzene. It has a vigorous reducing action on cold Fehling's solution, and is feebly alkaline towards turmeric; prolonged treatment with boiling water is without influence on the substance. The *hydrochloride* crystallises from a mixture of absolute alcohol and ether in hygroscopic leaflets; it begins to melt at 116°, and effervesces at 130°. When the aqueous solution is boiled in a reflux apparatus, the hydrochloride of triacetonedihydroxylamine anhydride is produced. The *oxalate*, prepared in the manner described, crystallises from dilute alcohol in small prisms; it melts and effervesces at 165°. The *dinitroso*-derivative, obtained by adding sodium nitrite to an aqueous solution of the hydrochloride, crystallises in leaflets, and is decomposed by concentrated caustic soda, which liberates gas. The compound is acidic in character, and does not reduce Fehling's solution; it fails to give Liebermann's reaction.

The *anhydride* of triacetonedihydroxylamine,

$$CO<\begin{matrix}CH_2\cdot CMe_2\cdot NH\\CH_2\cdot CMe_2\cdot NH\end{matrix}>O,$$

has been already described (*loc. cit.*), and is prepared by heating phorone with free hydroxylamine (2 mols.) and a few c.c. of concentrated caustic soda, in a reflux apparatus, until the liquid has no action on Fehling's solution; the *hydrobromide* and *hydriodide* crystallise in stellar aggregates of leaflets, the *oxalate* forms long needles, the *aurochloride* leaflets, and the *platinochloride* prisms.

When the dihydroxylamine derivative or its anhydride is reduced with zinc dust and hydrochloric acid, triacetonediamine is produced, identical with the compound obtained by Heintz from acetone and ammonia; the base boils at 95° under a pressure of 12 mm., and the aqueous solution, when boiled alone or with hydrochloric acid, yields triacetonamine. The *zinc* double salt crystallises from water in large plates containing water of crystallisation which is lost at 110°; it decomposes at 208°. The dioxalate crystallises in small white needles, and melts and effervesces at 189°.

If the reduction of the dihydroxylamine derivative and its anhydride is carried out with sodium amalgam and dilute sulphuric acid, *triacetonealkadiamine*, $NH_2\cdot CMe_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CMe_2\cdot NH_2$, is pro-

duced; this crystallises from ether in rhombic prisms, melts at 98—99°, and boils at 205—210°.

Triacetonehydroxylamine, $CO<\begin{smallmatrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{smallmatrix}>N\cdot OH$, is prepared by allowing phorone, dissolved in methylic alcohol, to remain with free hydroxylamine (1 mol.) and free sodium methoxide (1 mol.) for several days, until the reducing action of the liquid on Fehling's solution is but slight (compare *loc. cit.*); the *hydriodide* crystallises from a mixture of alcohol and ether in yellowish prisms, becomes brown at 170°, and melts at 180°. The *oxalate* also forms prisms, and melts at 85°. The *benzoyl* derivative crystallises from light petroleum in needles, and melts at 117°. Reduction with sodium amalgam in acid solution converts triacetonehydroxylamine into the *base*, $C_9H_{21}NO_2$, which crystallises in leaflets, melts at 56—57°, and boils at 225—235°; the *aurochloride* crystallises in lustrous, golden prisms. Triacetonehydroxylamine induces temporary paralysis of the spinal nerves.

Experiments on the behaviour of mesitylic oxide towards hydroxylamine have led to the production of three monhydroxylamine derivatives. M. O. F.

Ketonic Acetates. By A. Collet (*Compt. rend.*, 1897, **125**, 354—355. Compare Hunnius, Abstr., 1878, p. 147).—An alcoholic solution of the brominated ketone is warmed with a slight excess of pure dry potassium acetate, and after removal of the potassium bromide the alcohol is distilled off on the water bath and the residue poured into cold water. The oily product is then separated, dried, and distilled under diminished pressure.

a-Benzoylethylic acetate, $CH_3\cdot COO\cdot CHMeBz$, obtained from bromopropionyl benzene, is a yellow oil with an aromatic odour; it is insoluble in water, but dissolves in alcohol or ether; its sp. gr. = 1·11, and it distils at 158—160° under a pressure of 20 mm. *a-Benzoylpropylic acetate*, $CH_3\cdot COO\cdot CHEtBz$, boils at 164—170° under a pressure of 25—30 mm. *a-Benzoylisopropylic acetate*, $CH_3\cdot COO\cdot CHMe_2Bz$, boils at 135—140° (at 15—20 mm.).

When hydrolysed with dilute soda or with baryta water, these acetates yield yellow liquids having the characteristic properties of acetols. J. J. S.

Thio-organic Compounds of Arsenic. By N. Tarugi (*Gazzetta*, 1897, **27**, ii, 153—166).—At a low temperature and in presence of sufficient sodium carbonate to neutralise the hydrochloric acid produced, arsenic trichloride acts on thioacetic acid in accordance with the equation $2MeCOSH + AsCl_3 = (MeCOS)_2AsCl + 2HCl$. The *compound* of the composition $(MeCOS)_2AsCl$ is a yellowish liquid, of sp. gr. = 1·102, which begins to deposit arsenic trisulphide at 5°, and decomposes at lower temperatures on exposure to light; it is more stable when dissolved in alcohol, ether, chloroform, or carbon bisulphide.

On prolonged boiling, thioacetic acid and arsenic tri-iodide interact with formation of *arsenic sulphiodide*, AsSI, a crystalline, yellow powder insoluble in the ordinary solvents; it is decomposed by alkali hydroxides in accordance with the equation $3AsSI + 12NaHO = Na_3AsS_3 + 2Na_3AsO_3 + 3NaI + 6H_2O$, and is identical with the product

obtained by heating arsenic sulphide with iodine or arsenic trioxide. The reaction by which arsenic sulphiodide is produced, namely, $AsI_3 + MeCOSH + H_2O = AsSI + MeCOOH + 2HI$, is a reversible one.

At low temperatures, thioacetic acid reacts with arsenites in accordance with the equation $2MeCOSH + Na_3AsO_3 = (MeCO)_2S + NaAsOS + 2NaHO$; at ordinary temperatures, arsenic trisulphide is precipitated.

In presence of iodine and at a low temperature, thioacetic acid and arsenites react with formation of a heavy oil of the composition $(MeCOS)_2As_2S_3$; this is insoluble in water or organic solvents, slowly solidifies to a yellow mass, and when boiled with water yields acetic acid and arsenic trisulphide. This additive *compound* is also obtained by the action of acetic sulphide on arsenic trisulphide at ordinary temperatures. When the liquid substance is treated with gaseous ammonia, a compound of the composition $[MeCOS{\cdot}As(NH_2)]_2S_2$ is obtained as a yellow powder which is sparingly soluble in cold organic solvents, but dissolves in mineral acids with immediate precipitation of arsenic trisulphide; it is converted into a *substance* of the composition $[MeCOS{\cdot}As(OH)]_2S_2$ by suspending it in cool dilute acetic acid and adding potassium nitrite. On treating the additive compound with an alcoholic solution of aniline, a *substance* of the composition $[MeCOS{\cdot}As(NHPh)]_2S_2$ is obtained as a yellowish powder; a similar compound is obtained with paratoluidine. Both give the above dihydroxy-compound when treated with nitrous acid, and the toluidine derivative yields dehydrothiotoluidine when treated with dilute hydrochloric acid. W. J. P.

γ-Ketonic Acids. By Clemente Montemartini (*Gazzetta*, 1897, **27**, ii, 176—182).—On treating β-methyllevulinic acid with methylic iodide and sodium ethoxide, the author did not obtain ββ-dimethyllevulinic acid as was hoped, but a mixture of αβ-dimethylglutaric acid and methylsuccinic acid. On treating ethylic levulinate or α- or β-methyllevulinate with methylic iodide and sodium ethoxide, a mixture is ultimately obtained which can be separated into two substances boiling at 100—110° and 200—210°; the fraction boiling at 100—110° gives semicarbazones identical with those of the original materials in the case of the α- and β-methyllevulinates, but not in the case of ethylic levulinate. The *semicarbazone*, $C_8H_{15}N_3O_3$, of ethylic levulinate melts at 150°, whilst that from the ethylic levulinate recovered from the methylation melts at 141°; similarly, the respective *hydrazones* melt at 108° and 95—96°. The levulinic acid used was prepared from levulose and the discordant melting points are perhaps explained by Berthelot's observation (*Compt. rend.*, 1897, **123**, 341) that such levulinic acid is a mixture of two acids. W. J. P.

Dibasic Acids. By L. Étaix (*Ann. Chim. Phys.*, 1896, [vii], **19**, 356—407).—The author finds the best method of obtaining adipic acid to be Crum Brown and Walker's electrolytic method. *Adipic chloride*, $C_4H_8(COCl)_2$, after several fractionations under reduced pressure, forms a colourless liquid distilling at 125—128° under a pressure of 11 mm., but undergoing slight decomposition at the same time. *Adipic*

anhydride, $C_4H_8<\substack{CO\\CO}>O$, is obtained by the action of the chloride, diluted with a few cubic centimetres of anhydrous ether, on sodium adipate; it crystallises from benzene in small, mammillated masses melting at 95—100°; a small quantity of the same compound is obtained when adipic acid is boiled with acetic chloride for several hours. Adipic chloride reacts with benzene in the presence of aluminium chloride, yielding 1:6-*diphenylhexanedione*-1:6, $COPh\cdot[CH_2]_4\cdot COPh$, which crystallises from alcohol in yellowish needles melting at 102—103°; the corresponding *dioxime* melts at 216—218°. Ammonia reacts with a benzene solution of adipic anhydride, yielding adipamide and *adipamic acid*, the latter of which crystallises in microscopic needles melting at 125—130°.

The author has attempted to prepare diacetylpimelic acid, $CH_2(CHAc\cdot CH_2\cdot COOH)_2$, by the condensation of formaldehyde with acetopropionic acid in the presence of diethylamine, but without success.

Concise details are given for the separation of suberic and azelaic acids. *Suberic chloride*, $COCl\cdot[CH_2]_6\cdot COCl$, decomposes to a small extent when distilled under diminished pressure; it is an oil boiling at 162—163° under 15 mm. pressure; the anhydride (compare Anderlini, Abstr., 1894, i, 499) is obtained by the action of the chloride on sodium suberate and crystallises in minute needles melting at 65—66° (Anderlini, 62—63°). *Dibenzoylhexane* (1:8-*diphenyloctanedione*-1:8) melts at 83—85° and its *dioxime* at 192—193°. *ω-Benzoylheptoic acid*, $COPh\cdot[CH_2]_6\cdot COOH$, is also obtained in the preparation of the dibenzoyl compound; it crystallises in brilliant plates melting at 78°, and is but sparingly soluble in water. *Suberamide* melts at 216° and *suberamic acid*, obtained together with the amide by the action of dry ammonia on a benzene solution of the anhydride, crystallises in needles melting at 125—127° (compare Arppe, *Zeit. f. Chem.*, 1865, 300).

Azelaic chloride, $C_7H_{14}(COCl)_2$, is a colourless liquid boiling at 165° under a pressure of 13 mm., but is partially decomposed at the same time. The anhydride melts at 56—57° (Anderlini gives 52—53°). *Dibenzoylheptane*, $COPh\cdot[CH_2]_7\cdot COPh$, separates from alcohol in colourless crystals melting at 44°, and yields a *dioxime* which could not be obtained in a pure state. *Azelamide*, $CONH_2\cdot C_7H_{14}\cdot CONH_2$, melts at 172°, and *azelamic acid*, $CONH_2\cdot C_7H_{14}\cdot COOH$, at 93—95°.

Sebamic acid, $CONH_2\cdot[CH_2]_8\cdot COOH$ melts at 170°, and sebamide at 208°. The author points out that substituted succinic acids readily yield anhydrides, that oxalic, malonic, and substituted malonic acids do not yield anhydrides under any conditions, and that glutaric acid, substituted glutaric acids, adipic, suberic, azelaic and sebacic acids yield anhydrides, but not very readily. J. J. S.

Substituted Succinic Acids. By KARL AUWERS (*Annalen*, 1897, **298**, 147—181. Compare Abstr., 1896, i, 639).—The author has continued the investigation of asymmetric and symmetric methylethylsuccinic acids, and has established the identity of the former with isopimelic acid obtained from amylene bromide (compare *loc. cit.*).

Tertiary butylmalonic acid and the two stereoisomeric $\alpha\beta$-dimethylglutaric acids are the only members of the group of 24 isomeric acids having the formula $C_7H_{12}O_4$ which have not been yet characterised. (Compare Montemartini, Abstr., 1896, i, 667).

I. [With R. Fritzweiler].—The symmetrical methylethylsuccinic acids are prepared by the action of sodium on a mixture of ethylic methylmalonate and ethylic α-bromobutyrate, the details of the method, and the means by which the products are isolated, being described in the original paper. The fumaroid form crystallises from hot water in long, flat needles melting at 180° when heated with moderate rapidity, and at 177—179° when the temperature rises slowly; if rapidly heated, it melts at 182°, and water is eliminated at 190°. It dissolves readily in alcohol, ether, and acetone, and with difficulty in chloroform, being insoluble in petroleum; 3·05 parts dissolve in 100 parts of water at 17°. Metallic salts yield precipitates when added to a solution of the sodium salt, and calcium chloride gives rise to a crystalline salt when the liquid is boiled; the calcium salt obtained from the acid and calcium carbonate crystallises in colourless, anhydrous leaflets, being evidently different from the salt obtained by Bytschichin and Zelinsky, which contains $5H_2O$. The malenoid acid crystallises from water in stellate aggregates of slender, lustrous needles, melts at 101—102°, and loses water at 160°. It is readily soluble in organic solvents, excepting petroleum, which dissolves it with difficulty; 16·1 parts dissolve in 100 parts of water at 13°. Metallic salts give rise to precipitates, and calcium chloride produces a heavy precipitate in the cold solution, distinguishing this form from the fumaroid acid; the calcium salt contains $1H_2O$. The malenoid acid is obtained when the fumaroid modification is boiled for 3 hours, or heated at 210—220° during $8\frac{1}{2}$ hours; it is also produced in quantity amounting to 10 per cent. when the fumaroid acid is heated with 18 per cent. hydrochloric acid at 180—190° during 14 hours, the reverse action taking place with much greater readiness.

The *paratolilic acid* of the fumaroid acid crystallises from dilute alcohol in colourless, slender needles, and melts at 175—176°; the *paratolil* also forms needles, and melts at 109—110°. Another *compound* is produced when an attempt is made to prepare the tolil at high temperatures; it crystallises from petroleum, and melts at 86—89°. The *anilic acid* and *anil* melt at 164—165° and 103—104° respectively.

The *paratolilic acid* of the malenoid form crystallises from dilute alcohol in lustrous leaflets, and melts at 147—148°; the *paratolil* is identical with the derivative prepared from the fumaroid acid. The *anilic acid* and *β-naphthil* melt at 139—140° and 159—160° respectively; the *anil* is identical with the compound obtained from the fumaroid acid.

II. [With R. Fritzweiler].—Asymmetric methylethylsuccinic acid crystallises from water in transparent, lustrous prisms belonging to the rhombic system, and melts at 103—104°; in every particular, its properties agree with those ascribed to isopimelic acid, obtained by Bauer and Hell from amylene bromide. The *anilic acid* and *anil* melt at 168—169° and 60—61° respectively; the *paratolilic acid* and

paratolil melt at 162° and 64—65° respectively, whilst the *β-naphthilic acid* and *β-naphthil* melt at 179° and 96—97° respectively.

III. [With F. MAYER].—A specimen of amylene boiling at 29—35°, when converted into the bromide, then into the cyanide, and the latter hydrolysed, yielded a small proportion of isopropylsuccinic acid melting at 116°; the *paratolilic acid* crystallises from dilute alcohol, and melts at 143—144°.

IV. [With F. BETTERIDGE.]—*Ethylic α-bromolaurinate* is a colourless oil which boils at 170—174° under a pressure of 11 mm. When heated with finely divided silver at 150° during $5\frac{1}{2}$ hours, and the product hydrolysed, it yields *bidecylsuccinic acid*, the two isomerides being readily separable by petroleum. The *fumaroid* modification which dissolves but sparingly in petroleum, crystallises in white needles melting at 134°. The *malenoid* form is readily soluble, and separates in slender prisms melting at 74°. M. O. F.

Interconversion of Optical Antipodes. By PAUL WALDEN and O. LUTZ (*Ber.*, 1897, **30**, 2795—2798).—*l*-Bromo- or *l*-chloro-succinic acid, which yields *l*-malic acid when treated with silver oxide, undergoes a gradual change of rotation when it is heated with 12 per cent. methyl alcoholic ammonia at 40—45°. When the dextrorotation has attained a maximum (after 10—12 hours), a substance can be isolated which melts at 122—124°, and has $[\alpha]_D = +27{\cdot}6$ to $+29{\cdot}2°$ $(c = 20 - 1)$ in aqueous, $= +40{\cdot}8°$ in 75 per cent. alcoholic solution; the composition $O{<}{}^{CO-}_{NH_3}{>}CH{\cdot}CH_2{\cdot}COONH_4$ is assigned to it. By treating this with the equivalent quantity of dilute hydrochloric acid, the free acid can be obtained; this melts at 148°, and has the rotation $[\alpha]_D = +9{\cdot}7°(c = 3)$ in aqueous solution; the constitution,

$$CO{<}{}^{CH_2-}_{O\cdot NH_3}{>}CH{\cdot}COOH$$

is assigned to it; with ammonia, it regenerates the original compound. By boiling it, or its ammonium salt, with barium hydroxide, the barium salt of *d*-malic acid is obtained. In a similar manner, *l*-malic acid can be obtained from *d*-bromo- or *d*-chloro-succinic acid C. F. B.

Law of Etherification of Unsymmetrical Aliphatic Dicarboxylic Acids. By RICHARD ANSCHÜTZ (*Ber.*, 1897, **30**, 2652—2654. Compare following abstract).—Hydrogen α-ethylic mesaconate (*loc. cit.*), melting at 42°, obtained by the action of alcohol and hydrogen chloride on mesaconic acid, is readily hydrolysed by alkalis; the *β*-ethylic salt, however, which melts at 67—68°, yields the acid with difficulty when treated with hydrolytic agents. Its preparation from ethylic methylacetoacetate, by the introduction of 2 atoms of bromine followed by treament with barium carbonate and boiling water, indicates the constitution $COOEt{\cdot}CMe{:}CH{\cdot}COOH$, the α-salt being represented by the formula $COOH{\cdot}CMe{:}CH{\cdot}COOEt$.

The author therefore concludes that when etherification of an unsymmetrical dicarboxylic acid is effected by means of alcohol and hydrogen chloride, the alkylic radicle is introduced more readily into that carboxylic group which is attached to a tertiary carbon atom than into one combined with quaternary carbon. According to this

generalisation, the hydrogen orthoethylic and hydrogen alloethylic salts of camphoric acid are represented by the expressions,

$$\begin{array}{l} CH_2\cdot CH\cdot COOEt \\ \vert \qquad \rangle CMe_2 \\ CH_2\cdot CMe\cdot COOH \end{array} \quad \text{and} \quad \begin{array}{l} CH_2\cdot CH\cdot COOH \\ \vert \qquad \rangle CMe_2 \\ CH_2\cdot CMe\cdot COOEt \end{array}$$

respectively, a conclusion at which Bredt has already arrived from other data.

The author prefers the terms α-salt and β-salt to ortho- and allo- respectively, the α-salt being the one which is most readily produced.

M. O. F.

Preparation of Ethereal Salts. By RICHARD ANSCHÜTZ and JULIEN DRUGMAN (*Ber.*, 1897, **30**, 2649—2652. Compare E. Fischer and Speier, Abstr., 1896, i, 201).—The authors point out that the method of preparing ethereal salts described by Fischer and Speier (*loc. cit.*) can be advantageously modified by submitting the crude salt to direct distillation under considerably reduced pressure, excess of alcohol being previously removed by the same process.

Hydrogen α-methylic itaconate, $CH_2{:}C(COOH)\cdot CH_2\cdot COOMe$, crystallises from methylic alcohol and melts at 67°; it boils at 149° under a pressure of 12 mm.

Hydrogen α-ethylic itaconate melts at 45°, and boils at 153° under a pressure of 12 mm.

Hydrogen ethylic fumarate melts at 66°, and boils at 147° under a pressure of 16 mm.

Hydrogen α-methylic mesaconate, $COOH\cdot CMe{:}CH\cdot COOMe$, melts at 36°, and boils at 145° under a pressure of 15 mm.; *hydrogen α-ethylic mesaconate* melts at 42°, and boils at 150° under a pressure of 15 mm. *Hydrogen β-methylic mesaconate*, $COOMe\cdot CMe{:}CH\cdot COOH$, melts at 61—62°.

M. O. F.

δ-Methyluric Acid. By WOLF VON LOEBEN (*Annalen*, 1897, **298**, 181—187).—Three of the four theoretically possible methyluric acids have been already prepared, and in the case of two of these, the β- and γ-acids, the constitution has been recognised as that of 9-methyl-2 : 6 : 8-trioxypurine and 7-methyl-2 : 6 : 8-trioxypurine respectively (compare *Ber.*, 1897, **30**, 557). The α-methyluric acid, first obtained by Hill, is either 1-methyl-2 : 6 : 8-trioxypurine or 3-methyl-2 : 6 : 8-trioxypurine, whilst δ-methyluric acid is described in the present paper; the position of the methylic group in the latter acid, however, cannot be defined until the constitution of methylisodialuric acid, from which it is obtained by condensation with carbamide, has been determined.

Methylisodialuric acid, $C_5H_8N_2O_5$, prepared by oxidising methylisobarbituric acid with bromine water, is very readily soluble in water and separates in rosette-like aggregates. Barium hydroxide gives rise to a violet precipitate.

δ-Methyluric acid, $C_6H_6N_4O_3$, is obtained by heating methylisodialuric acid with carbamide and concentrated sulphuric acid at 100° and pouring the liquid into cold water; it separates from 500—600 parts of hot water in colourless, microscopic prisms containing $1H_2O$, which is removed at 150°. It gives the murexide reaction, and

oxidation with lead peroxide converts it into *methylallantoin*, $C_5H_8N_4O_3$ melting at 246°; the methylallantoin obtained by Hill from α-methyluric acid melts at 225°. δ-Methyluric acid dissolves in 527 parts of boiling water, α-methyluric acid requiring 262 parts. M. O. F.

Oximes of Hexahydrobenzophenone and Hexahydropropiophenone. By W. SCHARVIN (*Ber.*, 1897, **30**, 2862—2865. Compare Abstr., 1897, i, 612, where *for* 158° *read* 155° as the melting point of hexahydrobenzophenone α-oxime).—This α-oxime in ethereal solution reacts but slowly with phosphorus pentachloride, and the product is only slowly acted on by water; the final product was identified as benzoylhexamethyleneamine, $C_6H_{11}\cdot NH\cdot CPhO$ (von Baeyer, Abstr., 1894, i, 175). This is difficult to hydrolyse, but boiling with acetic anhydride converts it into acetylhexamethyleneamine. The β-oxime reacts much more readily with the pentachloride, and the product is readily converted by water into *hexahydrobenzanilide*, $C_6H_{11}\cdot CO\cdot NHPh$, together with some hexahydrobenzoic acid and aniline; this anilide is readily hydrolysed by strong sulphuric acid. In consequence of these reactions, the following configurations must be assigned to the two hexahydrobenzophenone oximes:

$$\begin{array}{c} C_6H_{11}\cdot \underset{\parallel}{C}\cdot Ph \\ OH\cdot N \end{array} \qquad\qquad \begin{array}{c} C_6H_{11}\cdot \underset{\parallel}{C}\cdot Ph \\ N\cdot OH \end{array}$$

α-Oxime. M. p. 155°. β-Oxime. M. p. 111°.

Hexahydropropiophenone, $C_6H_{11}\cdot COEt$, was obtained by the action of hexahydrobenzoic chloride (1 mol.) on zinc ethide (2 mols.); it boils at 195°, and does not form an additive compound with sodium hydrogen sulphite. Only one *oxime* could be obtained from it; this melts at 72—73°, and, in the Beckmann reaction, yields a product melting at 88°, which must be *propionohexamethyleneamide*, $C_6H_{11}\cdot NH\cdot COEt$, for it can be hydrolysed to propionic acid and hexamethyleneamine. The oxime must, therefore, have the configuration $\begin{array}{c} C_6H_{11}\cdot \underset{\parallel}{C}\cdot Et \\ OH\cdot N \end{array}$.

C. F. B.

The Benzene Nucleus. IX. By WILHELM VAUBEL (*J. pr. Chem.*, 1897, **56**, 266—271).—The author shows that the change of eugenol into isoeugenol, and also the structure of diketochlorides and allied substances described by Zincke (Abstr., 1897, i, 507), may be satisfactorily explained by his benzene configuration. A. W. C.

Anethoil and its Isomerides. By WILLIAM R. ORNDORFF, G. L. TERRASSE, and D. A. MORTON (*Amer. Chem. J.*, 1897, **19**, 845—870).—The authors, from a careful examination of anethoil and its isomerides, have arrived at the following conclusions.

(1) Eijkman's methylchavicole and Grimaux's estragole have the same molecular weight, and are metamerides of anethoil. The results of the investigation of these compounds by different chemists indicate their identity. (2) Liquid metanethoil also has the same molecular weight as anethoil; from its chemical behaviour, in which it closely resembles anethoil, and also from its physical properties, it is to be

regarded as a stereoisomeride of anethoil, and is probably the *trans*-compound, $\begin{array}{l}H\cdot C\cdot C_6H_4\cdot OMe\ (p)\\ \quad\ \| \\ Me\cdot C\cdot H\end{array}$ (3) Anisoin, the resinous polymeric modification of anethoil, acts as a colloid towards solvents such as ethylic acetate, acetone, and benzene. (4) Solid met-anethoil and the liquid isoanethoil both have a molecular weight twice that of anethoil, and hence should be named solid dianethoil and liquid dianethoil respectively. As they both behave like saturated compounds, they are possibly derivatives of tetramethylene. (5) By heating anethoil under pressure at 250—275°, it is transformed into isoanethoil, the methylic ether of paracresol and the methylic ether of parapropylphenol, the tendency under these conditions being apparently to form saturated compounds.

In determining the molecular weights of liquids such as anethoil by means of the boiling point method with the apparatus devised by Orndorff and Cameron (Abstr., 1895, ii, 480), the condenser tube was contracted a little below the point where the solvent condensed and ran back into the flask, so that when thin glass bulbs containing the liquid were dropped into the upper part of the condenser, they broke on reaching this point, or, if not, could be broken by means of a rod. This method is said to be more convenient and more accurate than that recommended by Beckmann.

The authors have also suggested names for anethoil and its isomerides more in accordance with the suggestions of the Geneva Conference and with the present state of knowledge. For example, liquid met-anethoil is named 1′-propenylphenol-4-methyl ether. E. W. W.

Action of Nitrogen Chloride on Aniline, Methylaniline, and Dimethylaniline. By W. Hentschel (*Ber.*, 1897, 30, 2643—2649). —When aniline is treated in molecular proportion with a solution of nitrogen chloride in benzene, a rise of temperature occurs, and trichloraniline is produced; this compound is also formed when chlorine is passed into aniline hydrochloride suspended in benzene. Acetanilide is converted into parachloracetanilide on agitation with a benzene solution of nitrogen chloride.

Trichloromethylaniline, $C_6H_2Cl_3\cdot NHMe$, is prepared by passing chlorine into benzene containing methylaniline hydrochloride in suspension, and is also formed when the base is treated with nitrogen chloride dissolved in benzene; it melts at 28·5°, and boils at 256°. The *hydrochloride* crystallises in prisms, and softens above 100°; the *platinochloride* forms large, pale-yellow crystals. Oxidation of trichloromethylaniline hydrochloride with a solution of chromic acid gives rise to trichloraniline, the azo-compound being produced when excess of the oxidising agent is employed; the azoxy-derivative is formed if the process is applied to warm solutions.

The action of nitrogen chloride on dimethylaniline yields a *compound*, $C_{24}H_{11}N_2Cl_{19}$, which crystallises from light petroleum and melts at 117°; it is insoluble in water, but is somewhat readily soluble in common organic solvents. When the compound is heated alone, hydrogen chloride is eliminated in quantity amounting to 18 per cent. of the substance taken. M. O. F.

Formation of Chains. XX. Chloranilines. XXI. Nitranilines. XXII. Nitrotoluidines. By Carl A. Bischoff (*Ber.*, 1897, **30**, 2760—2764; 2764—2768; 2769—2775. Compare this vol., i, 73).—The reacting substances, $C_6H_3R^IR^{II}\cdot NH_2$ (2 mols.) and $CHRBr\cdot COOEt$ (1 mol.), were heated for 4 hours at 100° (sometimes at 125—130°; the numbers referring to this temperature are given in brackets in the table below), and the percentage extent to which the condensation had taken place was estimated by weighing the hydrobromide, $C_6H_3R^IR^{II}\cdot NH_2,HBr$, that had separated, after washing it with warm ether. From the ethereal filtrate, unchanged amine could be removed by passing in gaseous hydrogen chloride and filtering, and from this second filtrate the product of the condensation was isolated by fractional distillation or by crystallisation. When the extent of the reaction was very small at the temperatures mentioned, special experiments were made at higher temperatures for the sole purpose of isolating some of the product. In the table below is given the percentage amount of condensation between the amines and ethereal α-bromo-salts there enumerated; the numbers for the methylanilines (toluidines) are taken from a previous investigation, and are inserted here for purposes of comparison.

Ethylic salt.	2-Chloraniline.	2-Methylaniline.	2-Nitraniline.	2-Nitro-4-methylaniline.	3-Chloraniline.	3-Methylaniline.	3-Nitraniline.	3-Nitro-4-methylaniline.	4-Chloraniline.	4-Methylaniline.	4-Nitraniline.	4-Nitro-2-methylaniline.
Bromopropionate	61	54	0 (14)	0 (7)	87	94	59 (87)	71 (88)	92	92	5(81)	0 (42)
Phenylacetate ...	49	43	42	17 (36)	71	47	77	84 (82)	72	43	63	45 (60)
Isobutyrate	9	19	0 (2)	(3)	21	62	9 (23)	(42)	23	38	0 (8)	(3)

The author draws attention to the effect of the different groups in the different positions, in promoting or hindering the condensation; it is impossible to quote his remarks in full, however, and the regularities are, moreover, apparent on inspection of the table given. Here, as often previously, substitution in the ortho-position is frequently found to hinder the condensation most, whilst in the meta-position it has the most favourable influence.

The following new ethylic salts are described :—*Chloranilido-α-propionates*, $C_6H_4Cl\cdot NH\cdot CHMe\cdot COOEt$: *ortho* boils at 280—285°, *meta* at 288—294° (melting at 40·3°), *para* at 300—306°. *Chloranilido-α-phenylacetates*, $C_6H_4Cl\cdot NH\cdot CHPh\cdot COOEt$: *ortho* melts at 53—54°, *meta* at 88—88·5°, *para* at 87·8°.—*Nitranilido-α-propionates*, $NO_2\cdot C_6H_4\cdot NH\cdot CHMe\cdot COOEt$, yellow; *ortho* melts at 142·5°, *meta* at 203°, *para* at 86—87°; *paranitranilido-α-propionic acid* (with H_2O) is yellow, melts at 147°, and is hygroscopic when anhydrous.

Nitranilido-α-phenylacetates, $NO_2\cdot C_6H_4\cdot NH\cdot CHPh\cdot COOEt$, yellow; *ortho* melts at 69—69·5°, *meta* at 83—84°, *para* at 120—120·5°. *Paranitranilido-β-isobutyrate*, $NO_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CHMe\cdot COOEt$, is yellow, and melts at 74°.—*Nitrotoluidido-α-propionates*,

$$NO_2\cdot C_6H_3Me\cdot NH\cdot CHMe\cdot COOEt,$$

[NO_2 : Me : NH = 3 : 1 : 4] yellow, melts at 62°; [2 : 1 : 4] at 64°; [5 : 1 : 2] at 103—104°. *Nitrotoluidido-α-phenylacetates*,

$$NO_2\cdot C_6H_3Me\cdot NH\cdot CHPh\cdot COOEt;$$

[3 : 1 : 4], yellowish-red, melts at 106°; [5 : 1 : 2], yellow, at 118·3°. *Nitrotoluidido-isobutyrate* [2 : 1 : 4] is yellowish and melts at 80°.

C. F. B.

Conversion of Amines into Phenols. By JACOB MEYER (*Ber.*, 1897, **30**, 2568—2569).—The observation that metaphenylenediamine evolved considerable quantities of ammonia and methylamine on methylation led to the general study of the behaviour of aromatic amines when treated with acids at high temperatures, and it was found that when the base was heated in a closed tube with either 1·15 per cent. hydrochloric acid, 20 per cent. sulphuric acid, solution of zinc chloride, &c., at 160—250°, a considerable quantity of the corresponding phenol was produced, the yield increasing with the temperature, although at high temperatures considerable quantities of resinous products were at the same time formed. Thus on heating 6 grams of metaphenylenediamine with 20 per cent. hydrochloric acid at 180°, 2 grams of resorcinol was produced, whilst from tetramethylmetaphenylenediamine 30 per cent. of resorcinol was obtained. J. F. T.

Derivatives of Paramidodimethylaniline [Dimethylparaphenylenediamine]. By JOHANNES PINNOW and E. KOCH (*Ber.*, 1897, **30**, 2860—2861).—When acetamidodimethylparaphenylenediamine is heated with methylic iodide in benzene solution for 10 hours at 100°, the acid radicle is not expelled, as in the case of the formamido-compound (Abstr., 1894, 281), but the compound $MeI,NMe_2\cdot C_6H_4\cdot NHAc$, melting at 226°, is formed. When this is treated with alcoholic lead acetate, the lead bromide first removed and then the rest of the lead by precipitation with hydrogen sulphide, and the filtrate finally evaporated down with hydrochloric acid, *trimethylparamidophenylium chloride hydrochloride*, $MeCl,NMe_2\cdot C_6H_4\cdot NH_2,HCl$, melting at 219°, is obtained; this has been used for the preparation of azo-dyes soluble in water.

C. F. B.

Combination of Metallic Acetates with Phenylhydrazine. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, **125**, 611—612).—Zinc, cadmium, manganese, and cobalt acetates combine with phenylhydrazine to form compounds of the formula $R,2N_2H_3Ph$ where R represents one molecule of the metallic acetate. Nickel acetate under similar conditions yields the compound $Ni(C_2H_3O_2)_2,3N_2H_3Ph$. The compounds are obtained by boiling the powdered salt with an alcoholic solution of phenylhydrazine for about 15 minutes and then filtering. The zinc compound forms rhomboidal plates which melt at 135°; the cadmium compound, elongated prisms melting at 121°; the manganese compound, monoclinic prisms melting at 97°; the cobalt compound crystallises in rose-coloured prisms which melt below

125°; and the nickel compound forms greenish-blue prisms which do not melt at 260°. All the salts decompose readily when heated. They dissolve in water, alcohol, or chloroform, but not in ether, and their solutions give the reactions of the metallic salt and phenylhydrazine.

C. H. B.

Combination of Phenylhydrazine with Metallic Salts. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, **125**, 714—716. Compare Abstr., 1897, i, 561, 562).—In addition to the compounds containing one molecular proportion of metallic salt and two molecular proportions of phenylhydrazine, nickel chloride, nickel sulphate, and cobalt bromide form compounds with 5 mols. of phenylhydrazine, whilst cobalt chloride and cobalt sulphate form compounds with 4 mols. They are obtained by the action of a large excess of phenylhydrazine on the metallic salt, and are only slightly soluble in alcohol or water in the cold and practically insoluble in ether or chloroform. They give the reactions of phenylhydrazine and the metallic salt that they contain, and they lose phenylhydrazine at 100°. $NiCl_2,5N_2H_3Ph$ forms long, blue, rhomboidal lamellæ, $CoCl_2,4N_2H_3Ph$ forms prismatic crystals, $CoBr_2,5N_2H_3Ph$ forms rhombic prisms, $CoSO_4,4N_2H_3Ph$ short prisms, and $NiSO_4,5N_2H_3Ph$ also crystallises in prisms.

Lithium chloride yields the compound $LiCl,2N_2H_3Ph$, which crystallises in deliquescent, rhomboidal lamellæ, and the halogen salts of the metals of the calcium group also yield compounds which will be described subsequently.

C. H. B.

Amidoazimidobenzene. By JOHANNES PINNOW and E. KOCH (*Ber.* 1897, **30**, 2850—2860).—Methylaniline was converted into dinitromethylaniline by nitration with a mixture of dilute nitric and sulphuric acids; this was reduced with alcoholic ammonium sulphide to nitroamidomethylaniline, $NO_2\cdot C_6H_3(NH_2)\cdot NHMe$, and this, by treatment with sodium nitrite in dilute nitric acid solution, was converted into nitromethylazimidobenzene, $NO_2\cdot C_6H_3{<}{\overset{\text{—N}}{\underset{\text{NMe}}{}}}{>}N$ (Zincke and Helmert, Abstr., 1896, i, 300). By reducing this with tin and hydrochloric acid, *amidomethylazimidobenzene*, $NH_2\cdot C_6H_3{:}N_3Me$, is obtained; this melts at 180°, the *hydrochloride* (with 2HCl), *hydrobromide*, *sulphate* (with $\frac{1}{2}H_2SO_4$) and yellow *picrate* (with $C_6H_3N_3O_7$) at 249°, 237°, 292°, and 237° respectively, the mono-*acetyl* and -*benzoyl* derivatives at 237° and 228·5°. The *carbamide*, $NH_2\cdot CO\cdot NH\cdot C_6H_3{:}N_3Me$ (from the hydrochloride and phenylic cyanate), *phenylcarbamide*,

$$NHPh\cdot CO\cdot NH\cdot C_6H_3{:}N_3Me,$$

and *phenylthiocarbamide* (from the base and phenylcarbimide or phenylthiocarbimide) were also prepared; of these, the last melts at 227—228°, the others remain unmelted at 300°. When amidomethylazimidobenzene hydrobromide (20 grams) is heated with methylic alcohol (22 grams) for 16 hours at 130—135°, yellow dimethylamidomethylazimidobenzene methobromide, $NMe_2\cdot C_6H_3{:}N_3Me,MeBr$, melting at 262°, is obtained; the corresponding *chloride* and yellow *picrate* melt at 205° and 169—170°. From the mother liquor of the bromide, by displacing the bromine by chlorine and adding mercuric chloride, a trimethylmethylazimido-

phenylium compound, $HHgCl_3,MeCl,NMe_2\cdot C_6H_3\dot{:}N_3Me$, melting at 195°, is obtained. If a relatively much smaller amount of methylic alcohol (0·8 gram per 5 grams of the hydrobromide) is used in the methylation, only a small quantity of a yellowish-brown nitroso-compound melting and decomposing at 150·5—151·5° (presumably methylazimidophenylmethylnitrosamine, $NO\cdot NMe\cdot C_6H_3\dot{:}N_3Me$), is formed when the product is treated with nitrous acid, so that the methylation probably begins with the addition of MeBr to the N_3Me group. *Dimethylamidomethylazimidobenzene* (*methylazimidodimethylaniline*), $NMe_2\cdot C_6H_3\dot{:}N_3Me$, is obtained by heating the above-mentioned methobromide with ammonia of sp. gr. = 0·91 for 9—10 hours at 180—185°, extracting with ether, evaporating the extract, dissolving the residue in hydrochloric acid, and precipitating with mercuric chloride; it melts at 90°, the *mercurochloride* (with $HCl,HgCl_2$) at 174—175°, and the *picrate* (with $2C_6H_3N_3O_7$) at 180—181°. By dissolving the base in hydrochloric acid, cooling the solution, and adding sodium nitrite, a nitro-derivative is obtained, *methylazimidonitrodimethylaniline*,

$$\begin{matrix}NO_2\\NMe_2\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}N\\NMe\end{matrix}\!\!>N\ [N:NMe:NMe_2:NO_2 = 2:3:5:6].$$

This is orange-red, and melts at 141°; dilute aqueous potash liberates dimethylamine, and acetic acid precipitates from the solution a yellowish-brown nitroso-compound melting at 191°, which is presumably methylazimidonitrophenylmethylnitrosamine. Reduction with zinc dust and acetic acid converts the nitro-compound into *methylazimidoamidodimethylaniline*, $NH_2\cdot C_6H_2(NMe_2)\dot{:}N_3Me$, the *zincochloride* of which (with $HCl,ZnCl_2$) melts at 276°; this base gives the phenazine reaction, from which it follows that the amido- and di-methylamido-groups must be in the ortho-position relatively to each other.

Both amidomethylazimidobenzene and its dimethyl-derivative yield colouring matters with diazobenzenesulphonic acid; in this respect, the substitution of methyl for imido-hydrogen in amidoazimidobenzene has had no effect. C. F. B.

Intramolecular Rearrangement of Isoaldoxime Ethers. By Carl Neubauer (*Annalen*, 1897, **298**, 187—201).—It has beeen shown that when the nitrogen benzyl ether of paranitrobenzaldoxime, in alcoholic solution, is heated with a very small quantity of sodium ethoxide, a part undergoes conversion into the nitrogen paranitrobenzyl ether of benzaldoxime, the action being reversible; a similar change on the part of the benzyl ether of metanitroisobenzaldoxime is, however, not reversible, whilst the benzyl ether of isoanisaldoxime is indifferent to the conditions described. The author has prepared other isoaldoxime ethers, and submitted them to the influence of alcoholic sodium ethoxide.

Benzylisocinnamaldoxime, $CHPh\dot{:}CH\cdot CH<\!\!\begin{matrix}N\cdot CH_2Ph\\|\\O\end{matrix}$, is obtained by heating cinnamaldehyde with β-benzylhydroxylamine hydrochloride (1 mol.) and sodium hydrogen carbonate in alcohol; it crystallises from dilute alcohol in lustrous, light yellow leaflets, and melts at 130°.

Benzylorthochlorisobenzaldoxime, $C_6H_4Cl\cdot CH<\overset{N\cdot CH_2Ph}{\underset{O}{|}}$, crystallises from petroleum in cubes, and melts at 86°.

Benzylorthonitroisobenzaldoxime, $NO_2\cdot C_6H_4\cdot CH<\overset{N\cdot CH_2Ph}{\underset{O}{|}}$, crystallises from very dilute alcohol in yellowish needles, and melts at 125—126°.

Benzylmetanitroisocinnamaldoxime,

$$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CH<\overset{N\cdot CH_2Ph}{\underset{O}{|}},$$

separates from benzene in yellow, lustrous leaflets, and melts at 123°.

Benzylparahydroxyisobenzaldoxime, $OH\cdot C_6H_4\cdot CH<\overset{N\cdot CH_2Ph}{\underset{O}{|}}$, crystallises from dilute alcohol in long, colourless needles, and melts at 203°.

β-Diparachlorodibenzylhydroxylamine, $(C_6H_4Cl\cdot CH_2)_2N\cdot OH$, is obtained by heating parachlorobenzylic chloride (2 mols.) in alcohol with hydroxylamine hydrochloride and sodium carbonate in a reflux apparatus; it crystallises from alcohol in white needles, and melts at 121—122°.

Parachlorobenzylparachlorisobenzaldoxime,

$$C_6H_4Cl\cdot CH<\overset{N\cdot CH_2\cdot C_6H_4Cl}{\underset{O}{|}},$$

is prepared from dichlorodibenzylhydroxylamine by oxidation with potassium dichromate and glacial acetic acid; it crystallises from alcohol in lustrous, white plates, and melts at 141°.

β-Parachlorobenzylhydroxylamine, $C_6H_4Cl\cdot CH_2\cdot NH\cdot OH$, obtained by passing steam into a solution of parachlorobenzylparachlorisobenzaldoxime in 20 per cent. hydrochloric acid, crystallises from light petroleum in beautiful, long needles, and melts at 87—88°. The *hydrochloride* melts at 165—166°.

Parachlorobenzylisobenzaldoxime, $CHPh<\overset{N\cdot CH_2\cdot C_6H_4Cl}{\underset{O}{|}}$, crystallises from dilute alcohol in rhombic leaflets, and melts at 125—126°.

Benzylparachlorisobenzaldoxime, $C_6H_4Cl\cdot CH<\overset{N\cdot CH_2Ph}{\underset{O}{|}}$, separates from dilute alcohol in long, prismatic needles, and melts at 121°.

Of the foregoing ethers, parachlorobenzylisobenzaldoxime and benzylparachlorisobenzaldoxime undergo molecular rearrangement.

A convenient method of preparing β-benzylhydroxylamine consists in heating a mixture of acetoxime and benzaldehyde (1 mol.) with an equal volume of 75 per cent. acetic acid in a reflux apparatus.

M. O. F.

Vinylideneoxanilide. By Hans von Pechmann (*Ber.*, 1897, **30**, 2791—2794).—This substance, $\begin{matrix}CO\cdot NPh\\ | \\ CO\cdot NPh\end{matrix}>C{:}CH_2$, which is formed when glyoxime-N-phenyl ether (Abstr., 1897, i, 75) is heated with acetic anhydride, is more conveniently prepared by boiling oxanilide with

acetic anhydride and sodium acetate. It melts at 208—210°, decolorises permanganate immediately, and reacts with bromine at 0° in chloroform solution; in the latter case, however, hydrogen bromide is given off, and the product, which melts at 189° and decolorises permanganate, is *bromovinylideneoxanilide*, $C_3N_2Ph_2O_2$:CHBr. Alcoholic hydrochloric acid decomposes it into its components, whilst alcoholic potash hydrolyses it to oxalic acid and ethenyldiphenylamidine, NPh:CMe·NHPh. Bromovinylideneoxanilide is hydrolysed by alcoholic potash to oxanilic acid, aniline, a little oxanilide, and presumably bromacetic acid. C. F. B.

Dyeing with "Substantive" Dyes. By Léo Vignon (*Compt. rend.*, 1897, **125**, 357—360).—As the result of various experiments, the author arrives at the following conclusions. The fixation of substantive dyes (for example, congo-red) on cotton is a chemical process, since the chemical composition of the dyes influences the fixation to a remarkable degree. Diamines (with the exception of orthophenylenediamine) and hydrazines are readily fixed, even when the amido-groups are substituted. Diphenyl, azobenzene, ammonia, hydroxylamine, and aromatic amines are not fixed. The dyeing of cotton is due to the presence of the group ⸗N·R·N⸗ or simply ⸗N·N⸗; it is probable that the fixing of the dye is due to the conversion of triad nitrogen into pentad, by the addition of cellulose molecules. This conclusion is supported by the fact that benzidene and tetramethylbenzidene, in both of which nitrogen is tervalent, can be fixed. But tetramethylbenzidene dimethyliodide, $C_6H_{12}(NMe_3I)_2$, in which nitrogen is quinquevalent, can not. J. J. S.

Some Organic Compounds containing Inorganic Radicles. By C. A. August Michaelis (*Ber.*, 1897, **30**, 2821—2822. Compare the following abstracts).—The radicles $SeCl_2$ and $TeCl_2$ can readily be introduced into various classes of organic compounds, the derivatives of the ketones, such as $(Ph·CO·CH_2)_2SeCl_2$ being of special interest. It is worthy of remark that the compounds of bismuth in which the metal is quinquevalent are more stable than those in which it is tervalent. A. H.

Organic Selenium Compounds. By C. A. August Michaelis and Franz Kunckell (*Ber.*, 1897, **30**, 2823—2828. Compare the foregoing abstract, and Abstr., 1895, i, 341).—*Selenonaphthyl methyl ether*, $(MeO·C_{10}H_6)_2Se$, obtained by adding selenyl chloride to an ethereal solution of α-naphthyl methyl ether, forms a crystalline mass melting at 138°. The corresponding β-compound crystallises in needles, melting at 162°. *Seleno-α-naphthyl ethyl ether* forms small, lemon-yellow needles, melting at 149°, whilst the β-compound crystallises in pure white needles, and melts at 176°. Selenyl chloride also reacts with phenols to form similar compounds. *Selenophenol*, $Se(C_6H_4·OH)_2$, forms a brittle, yellow mass soluble in alkalis. *Seleno-β-naphthol* crystallises in small plates, which have a reddish lustre and melt at 186°. *Selenylresorcinol*, $SeO[C_6H_3(OH)_2]_2$, has only been obtained in the form of a reddish-brown, brittle mass, which melts between 170° and 173°.

Selenium tetrachloride readily reacts with ketones to form compounds which still contain 2 atoms of chlorine. *Dichloroselenoacetone*

$(COMe{\cdot}CH_2)_2SeCl_2$, crystallises in white needles, which melt at 82° and emit a vapour which attacks the mucous membrane. It decomposes when kept, and is decomposed by boiling water, with separation of selenium. *Dichloroselenoacetophenone*, $(COPh{\cdot}CH_2)_2SeCl_2$, which is much more stable than the acetone derivative, crystallises in white needles; these melt at 122°, and can be preserved without undergoing any alteration. With dilute aqueous soda, this compound yields acetophenone and selenious acid, but when warmed with more concentrated soda, selenium is deposited. With phenylhydrazine, it yields a resinous mass. A. H.

Organic Tellurium Compounds. By E. Rust (*Ber.*, 1897, 30, 2828—2834. Compare the foregoing abstracts).—Tellurium tetrachloride crystallises from ether in long yellow needles containing 1 mol. of the solvent. *Dichlorotelluroanisoil*, $(OMe{\cdot}C_6H_4)_2TeCl_2$, obtained by the action of the tetrachloride on anisoil, crystallises in small, yellow needles melting at 190°. When its solution in hydrochloric acid is evaporated with platinum chloride, yellowish-brown needles of the *platinochloride*, $(OMe{\cdot}C_6H_4)_2TeCl_2,PtCl_4$, are obtained. *Dihydroxytelluroanisoil*, $(OMe{\cdot}C_6H_4)_2Te(OH)_2$, is obtained as an amorphous, white powder on dissolving the dichloro-compound in dilute aqueous soda and acidifying with acetic acid; when heated, it decomposes without melting and dissolves both in acids and alkalis. The *oxide*, $(OMe{\cdot}C_6H_4)_2TeO$, appears to be formed when the hydroxide is gently heated, but has not been obtained pure. *Dibromotelluroanisoil*, $(OMe{\cdot}C_6H_4)_2TeBr_2$, prepared by dissolving the hydroxide in hydrobromic acid, crystallises in yellow needles, and melts at 183·5°. *Di-iodotelluroanisoil*, crystallises in reddish-brown, lustrous plates, melting at 170°, whilst the *nitrate* forms colourless, compact crystals melting at 127—128°, and is soluble in water. *Dichlorotellurophenetoil*, $(OEt{\cdot}C_6H_4)_2TeCl_2$, crystallises in yellow needles, which melt at 185°. The *dihydroxy*-derivative is an amorphous, white powder; the *dibromo*-derivative crystallises in yellow needles melting at 183°. The *nitrate* crystallises in colourless plates, and melts at 120°. Tellurium tetrachloride combines with phenol in ethereal solution to form an *additive* compound, $TeCl_4,2PhOH$; this is a yellow, crystalline mass, which becomes brown at 182—183°. When the tetrachloride is heated with phenol, hydrogen chloride is evolved, but tellurium separates out. No crystalline products could be obtained by the action of the tetrachloride on naphthol, but with resorcinol, reaction takes place, and *dichlorotelluroresorcinol*, $[C_6H_3(OH)_2]_2TeCl_2$, is produced; this forms small, yellow crystals melting at 188—189°. The corresponding *dihydroxy*-compound is a white, amorphous powder. Like the corresponding selenium compound, tellurium tetrachloride readily reacts with ketones. *Dichlorotelluroacetophenone*, $(COPh{\cdot}CH_2)_2TeCl_2$, crystallises in slender, yellowish-white needles, which melt at 186—187°; potassium permanganate converts it into tellurous acid and chloracetophenone. The tetrachloride does not react with bromacetophenone. *Dichlorotelluroparanisyl methyl ketone*, $(OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2)_2TeCl_2$, crystallises in small, white needles melting at 190°. *Dichlorotelluroparatolyl methyl ketone* forms small, white needles melting and becoming green at 200°.

A. H.

Antimony Derivatives of Anisoil and Phenetoil. By CARL LÖLOFF (*Ber.*, 1897, 30, 2834—2843).—*Trianisylstibine*, $(OMe\cdot C_6H_4)_3Sb$, may be prepared by the action of sodium on a mixture of bromanisoil and antimony trichloride dissolved in benzene, or by the action of bromanisoil on an alloy of antimony and sodium. It crystallises in well-developed, colourless rhombohedra melting at 180·5—181°; hot concentrated hydrochloric acid converts it into anisoil and antimony trichloride. Alcoholic mercuric chloride added to its solution in chloroform, produces a white, crystalline precipitate of the *compound*, $(OMe\cdot C_6H_4)_3Sb,HgCl_2$, which decomposes without melting at 285°; when this is boiled with alcohol, it yields paranisylmercuric chloride, $HgCl\cdot C_6H_4\cdot OMe$ (Michaelis and Rabinerson, Abstr., 1890, 1269). *Trianisylstibine dichloride*, $(OMe\cdot C_6H_4)_3SbCl_2$, is formed when alcoholic cupric chloride is added to a chloroform solution of the stibine, cuprous chloride being also formed. It crystallises from benzene in large prisms with 1 mol. of the solvent; these melt at 82—83°, whilst the pure substance melts at 116—117°. *Trianisylstibine dibromide*, $(OMe\cdot C_6H_4)_3SbBr_2$, formed by the direct union of the stibine with bromine, crystallises in thin plates melting at 123°; it also separates from benzene in prisms containing 1 mol. of the solvent and melting at 81—82°. The *di-iodide* forms yellow, monosymmetric plates, which melt at 116°; the *nitrate*, which can be prepared by the action of silver nitrate on the bromide in alcoholic solution, crystallises in short, slender needles, which melt and decompose at 217°. *Trianisylstibine oxide*, $(OMe\cdot C_6H_4)_3SbO$, obtained by the action of alkalis on the halogen compounds, forms crystalline crusts melting at 191°; acids convert it into the salts described above.

Chlorine acts energetically on the stibine, resinous products being formed. When the chlorination is effected in a well-cooled chloroform solution, however, *dichloranisylstibine trichloride*, $(OMe\cdot C_6H_2Cl_2)_2SbCl_3$, is produced, which forms colourless crystals melting at 184°; trichloranisoil, $[OMe:Cl_3 = 1:2:4:6]$, is also produced in the reaction. *Dichloranisylstibic acid*, $(OMe\cdot C_6H_2Cl_2)_2SbO\cdot OH$, formed by the action of water on the foregoing compound, is a white, amorphous powder which melts and decomposes at 228—229°, and is insoluble in water and alcohol, but dissolves in aqueous soda and in alcoholic hydrogen chloride.

Triphenetylstibine, $(OEt\cdot C_6H_4)_3Sb$, crystallises in nodular aggregates of needles melting at 82—83°, and is decomposed by hydrochloric acid into phenetoil and antimony trichloride. The *mercurochloride*, $(OEt\cdot C_6H_4)_3Sb,HgCl_2$, is a white, crystalline, insoluble powder which decomposes at 225°. *Paratriphenetylstibine dichloride* crystallises with difficulty and melts at 84°; the *dibromide* crystallises in slender, asbestos-like needles melting at 110—111°; the *di-iodide* in prisms melting at 121—122°, whilst the *nitrate* separates in crystalline crusts which melt at 151—152°. The corresponding oxide could not be obtained. Chlorine produces a mixture of chlorinated diphenetylstibine chlorides, which are decomposed by water. A. H.

Some Aromatic Bismuth Compounds. By ARNOLD GILLMEISTER (*Ber.*, 1897, 30, 2843—2850. Compare the foregoing abstracts).—Bismuthtriphenyl does not appear to form a di-iodide, since when it is

acted on by iodine, or when the chloride is treated with potassium iodide, *bismuthodiphenyl iodide*, Ph_2BiI, is produced ; this crystallises in yellow needles melting at 133°, and is decomposed by alcohol, bismuthoxyiodide being formed. Bismuthotriphenyl is completely decomposed by a mixture of nitric and sulphuric acids, whereas the dichloride and the nitrate can readily be nitrated. *Bismuthodinitrotriphenyl dinitrate*, $(NO_2\cdot C_6H_4)_2PhBi(NO_3)_2$, obtained by the action of nitric and sulphuric acids on the nitrate, crystallises in flat, lustrous, yellowish prisms, which explode feebly at about 150°. The corresponding *dichloride* is precipitated when hydrochloric acid is added to a solution of the nitrate in acetic acid ; it crystallises in slender, white needles which melt at 136°, and detonate slightly when rapidly heated. *Orthobismuthotritolyl*, $Bi(C_6H_4Me)_3$, obtained by the action of orthobromotoluene on an alloy of bismuth with sodium, crystallises in colourless rhombohedra, which are isogonous with those of calc spar and melt at 128·5° ; it is decomposed by hot concentrated hydrochloric acid, toluene being formed. The *dichloride*, $(C_6H_4Me)_3BiCl_2$, formed by the direct combination of bismuthotritolyl with chlorine, forms white, rhombic crystals melting at 160°. The *dibromide* crystallises in yellow needles which melt at 125°, and gradually decompose on exposure to the air. The *nitrate* also forms rhombic crystals, and decomposes suddenly when heated.

Parabismuthotrixylyl, $(C_6H_3Me_2)_3Bi$, forms snow-white, matted needles which melt at 194·5° and are decomposed when heated with hydrochloric acid ; the *dichloride* melts at 167·5° and the *dibromide* at 130°. *Parabismuthotricumyl* forms lustrous, rhombohedral tablets melting at 159° ; the *dichloride* melts at 208°, and the *dibromide* at 150°. Pseudocumene and mesitylene derivatives could not be obtained. *Parabismuthotrianisyl*, $(OMe\cdot C_6H_4)_3Bi$, was obtained in small quantity from bromanisoil in the usual way. It forms lustrous cubes, melts at 190°, and is at once decomposed in the cold by hydrochloric acid. This compound is accompanied by *paradianisyl*, $(OMe\cdot C_6H_4)_2$, which crystallises in colourless, lustrous plates melting at 172°, and readily sublimes. Hydriodic acid converts it into paradiphenol. *Bismuthotrianisyl dibromide* crystallises in yellow needles melting at 103°, and is very stable. Chlorine converts the trianisyl compound into *bismuthotrichloranisyl dichloride*, $(OMe\cdot C_6H_3Cl)_3BiCl_2$, which melts at 133°. *Parabismuthotriphenetyl* forms monosymmetric prisms melting at 73°. No halogen derivatives could be obtained. A. H.

Halogen Derivatives of Phenyl Methyl Ketone. By A. Collet (*Compt. rend.*, 1897, **125**, 717—719).—Chloracetic chloride and bromacetic chloride in presence of aluminium chloride and carbon bisulphide act readily on chlorobenzene and bromobenzene, yielding dichloro-, dibromo-, or chlorobromo-derivatives of phenyl methyl ketone. *Parachlorophenyl chloromethyl ketone* melts at 101—102°. Gautier obtained the same compound by the action of chlorine on parachlorophenyl methyl ketone. *Parabromophenyl chloromethyl ketone* melts at 116—117° ; *parachlorophenyl bromomethyl ketone* at 96—96·5° ; and *parabromophenyl bromomethyl ketone* at 109—109·5°.

All these derivatives crystallise in slender, colourless needles and

dissolve in alcohol, especially on heating. When oxidised, the acetyl group is removed and parachloro- or parabromo-benzoic acid is obtained.

C. H. B.

Ethylic Quinoltetracarboxylic Acid from Ethylic Acetonedicarboxylic Acid. By HANS VON PECHMANN and LUDWIG WOLMAN (*Ber.*, 1897, **30**, 2569—2571).—After ethylic diacetylsuccinic acid had been synthesised by the action of iodine on the sodium compound of ethylic acetoacetate, a similar experiment was tried with the disodium compound of ethylic acetonedicarboxylate, and it was found that, under the conditions of experiment, 2 mols. of the disodium compound condensed, forming 4 mols. of sodium iodide and the corresponding diketohexamethylene compound. The latter, however, is oxidised at the moment of its formation by the free iodine present, and converted into ethylic quinoltetracarboxylic acid melting at 133—133·5°.

J. F. T.

Decomposition of Alkyl-sulphonates by Water, Acids, and Salts. By J. H. KASTLE, PAUL MURRILL, and JOS. C. FRAZER (*Amer. Chem. J.*, 1897, **19**, 894—901).—In continuation of Kastle and Murrill's previous work on the saponification of alkyl sulphonates by alcohols (Abstr., 1895, i, 370), the authors have determined the velocity of the decomposition of ethylic parabromobenzenesulphonate by water, alcohol, acids, and salts. In the case of water and aqueous solutions, complete mixture was effected by adding acetone. The progress of the action was determined from time to time by titrating with standard alkali, and in the case of the halogen acids and salts it was found necessary also to estimate the quantity of halogen which had not entered into reaction, by means of silver nitrate, since not only is the sulphonate decomposed by the water, but ethylic haloid is also formed. A. S. Loevenhart has obtained ethylic iodide in quantity by the action of potassium iodide on ethylic parabromobenzenesulphonate in solution in alcohol or acetone.

The velocity of the action in the case of water was found to be 3·5 times as great as for ethylic alcohol, whilst acids and salts were found to react much more rapidly than water alone. Rise of temperature causes a great increase in the velocity of decomposition, hydrochloric acid, for instance, at 98° effects as much decomposition in 20 minutes as it does in 10 days at the ordinary temperature. In some cases, the distribution of decomposition between the acid and the water was independent of temperature; with hydrochloric acid at the ordinary temperature, 72 per cent. of the sulphonate was decomposed by the acid and 16 per cent. by the water, whilst at 98°, 71 per cent. was decomposed by the acid and 16 by the water. Hydrochloric, hydrobromic, and hydriodic acid bring about the same amount of decomposition, and this is the case also with magnesium chloride and calcium chloride.

E. W. W.

Benzenesulphinic Acid as a Reagent. By OSCAR HINSBERG (*Ber.*, 1897, **30**, 2803—2805).—Benzenesulphinic acid (which has already been shown to unite with substances of quinonoid structure, forming sulphones; Abstr., 1896, i, 684) unites also with tetramethyldi-

amidobenzhydrol in dilute hydrochloric acid solution (when the latter substance must be formulated $NMe_2 \cdot C_6H_4 \cdot CH \colon C_6H_4 \colon NMe_2Cl$), yielding an additive compound, presumably

$$NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3(NMe_2) \cdot SO_2Ph.$$

This melts at 194°, is stable to acids and alkalis, and is oxidised by potassium permanganate and dilute sulphuric acid to a ketone that contains sulphur, presumably $NMe_2 \cdot C_6H_4 \cdot CO \cdot C_6H_3(NMe_2) \cdot SO_2H$.

C. F. B.

Paratoluenesulphinic Acid. By F. Arthur Hälssig (*J. pr. chem.*, 1897, **56**, 213—241. Compare next abstract, and Abstr., 1896, i, 684). —When ammonia is passed into a solution of paratoluenesulphinic acid in alcoholic or ethereal solution, the *ammonium* salt of the acid is obtained, which crystallises from alcohol in colourless needles melting and decomposing at 175°. If the reaction takes place in benzene solution, the ammonium salt of paratoluenesulphonic acid and paratoluenedisulphoxide are formed. Presumably, the ammonia acts first as a reducing agent, whereby 2 molecules of the sulphinic acid each give up a hydrogen and an oxygen atom, and the two SO groups become changed to $SO_2 \cdot S$, a third molecule becoming oxidised to the sulphonic acid.

Aromatic amines react with paratoluenesulphinic acid, giving salts which, when strongly heated, yield blue to red violet resins, from which the colouring matters could not be isolated. The *aniline* salt crystallises in colourless needles melting at 118°; the *orthotoluidine* salt in colourless needles melting at 124°; the *paratoluidine* salt in needles melting at 140°, and the *metaxylidene* salt in white needles melting at 129·5°. With *phenylhydrazine, a salt* is obtained as colourless, asbestos-like needles melting at 159—160° with decomposition; and with *hydrazine hydrate, a salt* as glistening leaflets melting partially at 107°, and decomposing entirely at 140°.

Phenylparatoluenesulphazide, $C_6H_4Me \cdot SO_2 \cdot NH \cdot NHPh$, is prepared by the action of phenylhydrazine on paratoluenesulphonic chloride; it crystallises from alcohol in beautiful needles melting and decomposing at 155°. When treated with sodium hydroxide, it is converted into benzene, nitrogen, water, and sodium paratoluenesulphinate; at the same time, a red, crystalline substance melting at 65° is obtained, but in quantity too small for further investigation. The same sulphazide is also produced together with paratoluenedisulphoxide when paratoluenesulphinic acid is acted on with phenylhydrazine hydrochloride.

By the action of hydrazine hydrochloride on paratoluenesulphinic acid, paratoluenedisulphoxide is obtained, together with a *substance* crystallising from alcohol in clear needles and melting at 180·5° with decomposition. Its aqueous solution reacts feebly acid, and reduces ammoniacal silver nitrate at ordinary temperatures. It yields a *benzoyl* derivative crystallising from alcohol in needles melting and decomposing at 209·5°, but the constitution of this substance has not so far been satisfactorily determined. Phenylmethylhydrazine and paratoluenesulphinic acid give rise to a *salt* crystallising from alcohol in silken needles melting at 126°; this, when treated with hydrochloric acid, is transformed into a *substance* of the composition $C_{28}H_{34}S_2O_3N_4$. Neither by this re-

action nor by the action of phenylmethylhydrazine on paratoluenesulphonic chloride could the corresponding sulphazide be obtained.

Free hydroxylamine reacts with paratoluenesulphinic acid, giving rise to paratoluenesulphonamide, and the hydroxylamine salt of the acid as an intermediate product. The action with β-dibenzylhydroxylamine is complex; the products are benzaldehyde, paratoluenedisulphoxide, benzylisobenzaldoxime, *paratoluenesulphinic acid β-benzylhydroxylamine* forming mother-of-pearl, glistening leaflets melting at 176°, and the *β-dibenzylhydroxylamine* salt as small crystals melting at 156°.

By melting acetoxime or α-benzaldoxime with paratoluenesulphinic acid, the ammonium salt of the acid and paratoluenesulphonamide are produced; but if the action take place in acetic acid solution, with acetoxime, paratoluenedisulphoxide and ammonium paratoluenesulphonate are formed, and with benzaldoxime a *condensation* product insoluble in alcohol, ether, and benzene, and soluble only with decomposition in acetic acid; it melts at 124°, and is converted by dilute alkalis into benzaldehyde, paratoluenesulphonamide, and paratoluenesulphinic acid.

A. W. C.

Derivatives of Paratoluenesulphinic Acid. By ERNST VON MEYER (*J. pr. chem.*, 1897, **56**, 272. Compare preceding abstract, and Abstr., 1896, i, 684).—A preliminary note on the compounds formed by the action of certain diazo-compounds on paratoluenesulphinic acid. The *substance*, $N_2Ph\cdot SO_2\cdot C_6H_4Me$, forms beautiful, yellow crystals melting at 94·5°. When acted on by aniline, methyl-, or dimethylaniline or quinoline in alcoholic solution, it is converted into a *substance* of the composition $C_{20}H_{20}S_2O_4N_2$, which is probably *diparatolylsulphone phenylhydrazine*; this forms white needles melting at 198°.

A. W. C.

A Transformation of Tetrahydropyrone Derivatives. By PAWEL IW. PETRENKO-KRITSCHENKO and D. PLOTNIKOFF (*Ber.*, 1897, **30**, 2801—2803).—When acetonedicarboxylic acid is mixed with three times the quantity of benzaldehyde, the product shaken with dilute soda, and the solution, after being freed from excess of benzaldehyde by extraction with ether, is acidified, *diphenyltetrahydropyronedicarboxylic acid*, $CO<\begin{matrix}CH(COOH)\cdot CHPh\\CH(COOH)\cdot CHPh\end{matrix}>O$, separates as a semi-solid mass. It gradually loses carbonic anhydride, and the product is *diphenyltetrahydropyrone*, $CO<\begin{matrix}CH_2\cdot CHPh\\CH_2\cdot CHPh\end{matrix}>O$; this melts at 131°. When its alcoholic solution is warmed with a few drops of hydrochloric acid, dibenzylideneacetone, $CO(CH{:}CHPh)_2$, is formed. C. F. B.

Action of Tetrazodiphenyl Chloride on Benzene. By E. CASTELLANETA (*Ber.*, 1897, **30**, 2799—2801).—Tetrazodiphenyl chloride, $Cl\cdot N_2\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot Cl$, is prepared by dissolving benzidine in absolute alcohol, passing in gaseous hydrogen chloride, adding amylic nitrite at 5°, and then ether; it explodes at 106—108° or when struck, and keeps well in the dry state. When it is heated on the water bath with excess of benzene and a little aluminium chloride, it yields a mixture of *parachloroparadiphenylbenzene*, $C_6H_4Cl\cdot C_6H_4Ph$, melting at 220—220·5°, with paradichlorodiphenyl, $C_6H_4Cl\cdot C_6H_4Cl$, the latter of

which is rather more soluble in alcohol than the first; no biphenyldiphenyl, $C_6H_4Ph \cdot C_6H_4Ph$, is formed. C. F. B.

Aromatic Hydroxyketones. By EMILIO NOELTING and ALFRED MEYER (*Ber.*, 1897, **30**, 2590—2595).—2 : 3 : 4 : 3′ : 4′-*Pentahydroxybenzophenone*, $C_6H_2(OH)_3 \cdot CO \cdot C_6H_3(OH)_2$, obtained by heating protocatechuic acid with pyrogallol and zinc chloride at 140—145°, crystallises with $2H_2O$ in slender, light yellow needles, and melts when dry at 192—193°. Concentrated sulphuric acid converts it into protocatechuic acid and decomposition products of pyrogallol.

An *isomeric* compound, $[(OH)_5 = 3 : 4 : 5 : 3' : 4']$, is produced when gallic acid is heated with catechol and zinc chloride; it also crystallises in light, yellow needles with $2H_2O$, but melts at 266°; like its isomeride, it yields protocatechuic acid when heated with sulphuric acid. This reaction shows the constitution of the two compounds.

2 : 4 : 3′ : 4′-*Tetrahydroxybenzophenone*, $CO[C_6H_3(OH)_2]_2$, obtained from protocatechuic acid and resorcinol, forms brownish-yellow crystals containing $2H_2O$, and melts at 199°. 2 : 3 : 4-*Trihydroxyphenyl* 3-*hydroxy-β-naphthyl ketone*, $OH \cdot C_{10}H_6 \cdot CO \cdot C_6H_2(OH)_3$, is prepared from β-hydroxynaphthoic acid and pyrogallol; it forms small, yellow crystals melting at 287—289°. When heated with resorcinol and zinc chloride, β-hydroxynaphthoic acid yields a substance which is probably a mixture of the ketone with hydroxyxanthone formed from it by loss of water. Pentahydroxy- and tetrahydroxy-benzophenone have been previously described in the German Patent No. 72446, belonging to the Höchst company. A. H.

New Method of obtaining Colouring Matters of the Malachite-Green Series. By EMILIO NOELTING (*Ber.*, 1897, **30**, 2588—2590).—Benzanilide and its derivatives usually react with tertiary aromatic amines in presence of phosphorus oxychloride to form derivatives of dialkylamidobenzophenones. (German Patent, 41751). When, however, a hydroxy-group is present in the ortho-position in the benzoic acid residue the reaction takes another course, and a compound of the malachite-green series is produced. Thus salicylanilide and dimethylaniline react to form a green *colouring matter* which on reduction yields the leuco-base obtained by O. Fischer from salicylaldehyde and dimethylaniline (Abstr., 1882, 392). Orthocresotic anilide yields a similar *compound*, whereas the anilides of meta- and parahydroxybenzoic acid and of orthonitro- and orthamido-benzoic acid yield no compound of this class. A green colouring matter is also formed from the anilide of orthohydroxynaphthoic acid. A. H.

Paradinitrodibenzyldisulphonic Acid. By CHRISTOPH RIS and CARL SIMON (*Ber.*, 1897, **30**, 2618—2620).—Sodium paradinitrodibenzyldisulphonate can readily be prepared by the action of aqueous soda and sodium hypochlorite on sodium paranitrotolueneorthosulphonate; it crystallises in colourless needles, and deflagrates at a high temperature. Alkalis convert it into yellow substances, and it appears probable that the yellow substance described by Bender (Abstr., 1895, i, 287) as potassium paradinitrodibenzyldisulphonate is in reality such a decomposition product. A. H.

Anilineazo-α-Naphthol. By OTTO N. WITT and JENS DEDICHEN (*Ber.*, 1897, **30**, 2655—2667. Compare Abstr., 1894, i, 606).—In many respects the behaviour of anilineazo-α-naphthol is inconsistent with the view that it is the exact analogue of hydroxyazobenzene. Its resistance to ordinary methods of alkylating phenols, for instance, and the pronounced basic character of the colouring matter and its ethers, serve to differentiate it from the type in question.

The general method of preparing azo-colouring matters is not the most suitable for the production of anilineazo-α-naphthol, as the unmodified process gives rise also to a disazo-compound; this bye-product is not formed, however, if the operation is carried out in alcoholic solution. An ice-cold solution of diazobenzene chloride, prepared from 93 grams of aniline dissolved in 200 c.c. of concentrated hydrochloric acid and 250 c.c. of water, is added to a cooled solution of 155 grams of α-naphthol in 2000 c.c. of alcohol, anilineazo-α-naphthol hydrochloride being slowly deposited from the liquid; the azo-compound is obtained by dissolving the hydrochloride along with potassium acetate in boiling glacial acetic acid, from which it separates in reddish-brown crystals with green reflex. It melts at 206°. The potassium derivative forms large, reddish-brown crystals, with feeble metallic lustre.

The *compound*, $C_{32}H_{22}N_4O_2$, arising from elimination of two hydrogen atoms from 2 molecules of anilineazo-α-naphthol, is prepared by the action of oxidising agents such as ferric chloride and potassium dichromate, which when added to a solution of the potassium derivative, precipitate a mixture of unaltered colouring matter and the product of its oxidation; it is also obtained by the action of nitrosodimethylaniline, and by protracted treatment with boiling glacial acetic acid, in which it is insoluble. (Compare Fischer and Hepp, Abstr., 1892, 1476.) The substance forms deep red crystals, and melts and decomposes at 245—246°; it is insoluble in ordinary media, and is devoid of basic properties. The solution in cold concentrated sulphuric acid is violet. The *acetyl* derivative crystallises from toluene in lustrous, orange-red, dichroic needles, and melts at 264—265°.

When the oxidation product from anilineazo-α-naphthol is reduced with tin and hydrochloric acid, diparamidonaphthol is produced, and when the hydrochloride of this base is oxidised with concentrated nitric acid, *dinaphthaquinone*, $C_{20}H_{10}O_4$, is obtained; it begins to decompose at 270°, and yields β-dinaphthyl when heated with zinc dust. The compound obtained by oxidising anilineazo-α-naphthol, therefore, has the constitution $NPh\colon N\cdot C_{10}H_5(OH)\cdot C_{10}H_5(OH)\cdot N\colon NPh$.

It has been already stated that the new colouring matter forms a violet solution in concentrated sulphuric acid. If the liquid is gently heated it becomes blue, and when poured into water yields a dark brown precipitate, which becomes orange on treatment with soda; the *compound*, $C_{32}H_{20}N_4O$, obtained by this method is purified by precipitating its solution in phenol with alcohol, and subsequently crystallising from boiling xylene. It forms lustrous, orange-red crystals, and melts at 290—291°, when decomposition begins; the substance is insoluble in dilute acids and alkalis, and the solution in concentrated sulphuric acid is blue. Reduction converts it into the crystalline hydrochloride of a new compound.

M. O. F.

A General Reaction of Aromatic Quinones. II. By SIEGFRIED BLUMENFELD and PAUL FRIEDLÄNDER (*Ber.*, 1897, **30**, 2563—2568. Compare Abstr., 1897, i, 473).—There are only two possible ways of formulating a substance formed by the condensation of a quinone with a phenol without elimination of water, for either the product is a hydroxy-derivative of a hydrocarbon, or the two rings are joined by means of oxygen, thus forming a hydroxy-derivative of an ether; for instance, the product of condensation of α-naphthaquinone with pyrogallol may be either a pentahydroxyphenylnaphthalene or a tetrahydroxyphenyl naphthyl ether. Since, on investigation, this compound was found to yield a tetracetyl derivative, the latter formula is evidently the correct one. 2 : 3-*Dihydroxyphenyl* 1 : 4-*dihydroxy*-2-*naphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_6H_3(OH)_2$, formed by the condensation of α-naphthaquinone with pyrogallol in glacial acetic acid solution, crystallises from the latter in pale grey needles melting and decomposing at 240—246°, the *tetracetyl* derivative crystallises from glacial acetic acid in colourless needles melting at 165—170°, whilst the *benzoyl* derivative forms white needles melting at 203—205°. *Dihydroxydi-α-naphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_{10}H_7$ $[(OH)_2 : O = 1 : 4 : 2]$, formed by the condensation of α-naphthaquinone with α-naphthol, crystallises in colourless needles melting at 240—245°, the *diacetyl* derivative crystallises from glacial acetic acid and softens at 240°, remaining, however, solid at 300°.

β-Naphthaquinone, on condensation with pyrogallol, yields 2 : 3-*dihydroxyphenyl* 1 : 2-*dihydroxynaphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_6H_3(OH)_2$, which, after recrystallisation, melts at 242—245°, and the *tetracetyl* derivative at 184—188°; with α-naphthol, β-naphthaquinone yields 1 : 2-*dihydroxydinaphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_{10}H_7$, which does not show a sharp melting point the *diacetyl* derivative melts at 220°. β-Naphthaquinone and resorcinol produces 3-*hydroxyphenyl* 1 : 2-*dihydroxynaphthyl ether*, $C_{10}H_5(OH)_2 \cdot O \cdot C_6H_4 \cdot OH$; this separates from its glacial acetic acid solution on dilution with water and melts at 236—240°. The *triacetyl* derivative melts at 169—170°.

Benzoquinone combines with α-naphthol and resorcinol, forming in the first case *trihydroxydiphenyl ether*, $C_6H_3(OH)_2 \cdot O \cdot C_6H_4(OH)$ $[(OH)_2 : O : OH = 1 : 4 : 1' : 3']$, which crystallises with difficulty and yields a *benzoyl* compound which separates from alcohol in white needles melting at 188—191°. J. F. T.

Isomeric Change of Dihydrocarvone into Carvenone. By IWAN L. KONDAKOFF and TH. GORBUNOFF (*J. pr. chem.*, 1897, **56**, 248—257).—When a solution of $\Delta_{8,9}$-dihydrocarvone in light petroleum is saturated with hydrogen bromide, the former substance is converted into carvenone. During the reaction a small amount of a bromo-derivative is formed, which, on treatment with zinc dust, is completely converted into the same carvenone, boiling at 232—233° at 758 mm. It has a sp. gr. = 0·921 at 20°/20°, and a refractive index $n_D = 1·47664$ at 20°, corresponding with a molecular refractive index of 46·63 (calculated 46·76).

Dihydrocarvone takes up the elements of hydrogen chloride when treated with the latter in acetic acid solution. The *chloroketone* formed boils at 155·5—157° at 15 mm.; has a sp. gr. = 1·0266 at 20°/20°; a

refractive index $n_D = 1{\cdot}47877$, and is lævorotatory; $a_D = -11{\cdot}72$. When heated on the water bath for 2 hours with alcoholic soda, it loses completely the elements of hydrogen chloride, yielding *carone* boiling at 101—102° at 15 mm. It has a sp. gr. $= 0{\cdot}9575$ at 21°/21°; a refractive index $n_D = 1{\cdot}47664$, and is dextrorotatory; $a_D = +174{\cdot}36°$. It is readily oxidised on treatment with potassium permanganate. The investigation is proceeding. A. W. C.

Menthonecarboxylic Acid and Menthonedicarboxylic Acid. By GIUSEPPE ODDO (*Gazzetta*, 1897, **27**, ii, 97—116).—On treating menthone in absolute ethereal solution with sodium wire, a large part of the metal is rapidly dissolved, whilst the remainder only dissolves on prolonged ebullition; 1 atom of sodium requires $1\frac{1}{5}$ molecules of menthone for its solution. The liquid is saturated with carbonic anhydride, cooled with powdered ice, and the two layers separated; the ethereal solution, besides menthol and menthone, contains Beckmann's menthopinacone (Abstr., 1897, i, 248). On acidification with hydrochloric acid, the aqueous layer deposits an oil which can be extracted with ether; the ethereal solution, on evaporation, yields a mixture from which light petroleum extracts menthonecarboxylic acid, and leaves Brühl's menthonedicarboxylic acid (Abstr., 1892, 200). The petroleum extract is washed with sodium carbonate solution, and the latter acidified and extracted with ether; on evaporating this ethereal solution, menthonemonocarboxylic acid is obtained.

Menthonecarboxylic acid, $\begin{array}{l} CH_2{\cdot}CHMe{\cdot}CH{\cdot}COOH \\ CH_2{\cdot}CHPr{\cdot}CO \end{array}$, is a heavy, colourless, nearly odourless oil, which yields menthone when heated with dilute sulphuric acid; it is sparingly soluble in water, and its solution turns violet with ferric chloride. The *silver* salt, $C_{10}H_{17}O{\cdot}COOAg$, is a flocculent, white precipitate. On treating the acid with sodium nitrite and acid at ordinary temperatures, *isonitrosomenthone*, $\begin{array}{l} CH_2{\cdot}CHMe{\cdot}C{:}NOH \\ CH_2{\cdot}CHPr{\cdot}CO \end{array}$, is obtained, together with a reddish oil insoluble in alkalis, which is probably an *orthodiketone* of the constitution $\begin{array}{l} CH_2{\cdot}CHMe{\cdot}CO \\ CH_2{\cdot}CHPr{\cdot}CO \end{array}$; isonitrosomenthone is an oil which gives a yellow solution in alkalis. On reduction with zinc dust and acetic acid in dilute alcoholic solution, it yields *menthoneamine*, $\begin{array}{l} CH_2{\cdot}CHMe{\cdot}CH{\cdot}NH_2 \\ CH_2{\cdot}CHPr{\cdot}CO \end{array}$, as an oil smelling like camphoramine; the *hydrochloride* crystallises in colourless prisms melting at 181—183°, and the *platinochloride* in red prisms which melt and decompose at 175—180°; apparently it yields thymol on heating.

Menthonedicarboxylic acid, which has the constitution

$$\begin{array}{l} CH_2{\cdot}CHMe{\cdot}C(COOH)_2 \\ CH_2{\cdot}CHPr{\cdot}CO \end{array} \quad \text{or} \quad \begin{array}{l} CH_2.CHMe\text{———}CH{\cdot}COOH \\ CH_2{\cdot}CPr(COOH){\cdot}CO \end{array},$$

melts at 140—141° with decomposition, not at 128·5°, as stated by Brühl (*loc. cit.*); when treated with diazobenzene chloride, it yields a *compound* which crystallises in dark-red crystals melting at 126—128°. W. J. P.

Borneols and their Ethers. By JULES MINGUIN (*Compt. rend.*, 1896, **123**, 1296—1298).—A method is described for separating dextroborneol from lævoisoborneol in the mixture obtained by the reduction of camphor.

The author is of opinion that the phenomenon observed by Montgolfier on the etherification of a mixture of dextroborneol and lævoisoborneol, and on subsequent hydrolysis, namely, an increase in the dextrorotatory power, is not due to a partial conversion of the *l*-isoborneol into *d*-borneol, but is due to the fact that borneol is more readily etherified than isoborneol. J. J. S.

Camphoquinone. By OTTO MANASSE and ERNST SAMUEL (*Ber.*, 1897, **30**, 3157—3161. Compare Abstr., 1897, i, 290).—The *acid* $C_{10}H_{16}O_3$ is obtained by dissolving finely-powdered camphoquinone in 15 parts of concentrated sulphuric acid, which is cooled and agitated during the process; after a short interval, the new substance is precipitated by pouring the liquid on to ice. It dissolves with great difficulty in cold water, but is soluble in 20 parts at 60°, separating from the solution in slender needles melting at 67—68°; it contains $1H_2O$, which is removed in the desiccator or on exposure to a temperature of 50°, the anhydrous acid, which is very hygroscopic, melting at 97—98°. The acid is readily soluble in common organic solvents, excepting petroleum, from which it crystallises in long, slender needles melting at 97—98°; it is monobasic in character, and exhibits the properties of an aldehyde or ketone, producing a metallic mirror when boiled with water and silver oxide, and developing a reddish-violet coloration with a sulphurous acid solution of magenta. It is somewhat stable towards potassium permanganate, and resists the action of boiling 50 per cent. sulphuric acid, but is readily oxidised by a solution of bromine in caustic soda. The *oxime* crystallises from chloroform in glistening leaflets, and melts at 163—164°; it is readily soluble in acids and alkalis, but dissolves with some difficulty in water. The *phenylhydrazone* crystallises from dilute alcohol, and melts at 123—124°. The *semicarbazone* separates from alcohol as a microcrystalline powder and melts at 217—218°; it dissolves readily in sodium carbonate, and the alcoholic solution reddens litmus.

When camphoquinone is exposed to the vapour of bromine, it is converted into the *compound*, $C_{10}H_{11}Br_3O_3$, which crystallises from benzene in lustrous prisms and melts at 197—198°. If bromination is carried out by adding bromine to the quinone until action ceases, and heating the product on the water bath, the *compound*, $C_{10}H_{12}Br_2O_3$, is produced; this, which crystallises from alcohol in long, lustrous needles, and melts at 137—138°, is not identical with π-dibromocamphoric anhydride. M. O. F.

Camphor Compounds. By GIUSEPPE ODDO (*Gazzetta*, 1897, **27**, ii, 117—131).—On heating camphoquinone with hydrazine hydrochloride in acetic acid solution, *biscamphanonazine*,

$$C_8H_{14}<\begin{matrix}C{:}N\cdot N{:}C\\ | \qquad\quad | \\ CO \qquad CO\end{matrix}>C_8H_{14},$$

is obtained; it crystallises in colourless scales melting at 217—218°,

is hydrolysed by fuming hydrochloric acid, and is identical with Angeli's azocamphanone (Abstr., 1895, i, 61).

Camphoquinone and hydriodic acid do not react in presence of red phosphorus at 115—125°, but at 150° the quinone is wholly converted into camphoric acid.

Bromocamphocarboxylic acid does not react with nitrous acid, but, under similar conditions, camphocarboxylic acid yields isonitrosocamphor (Abstr., 1893, i, 422); the bromo-acid should therefore contain the group –CBr(COOH)·CO– and its ready conversion into bromocamphoric acid indicates that the bromine is attached to the same carbon atom in both acids.

α-Dibromocamphor is converted by sodium in boiling ethereal solution into monobromocamphor and a *dibromodicamphor*, $C_{20}H_{30}Br_2O_2$; the latter crystallises in thin, white needles melting at 128—129°, and slowly decomposes with evolution of hydrogen bromide. Under similar conditions, β-dibromocamphor loses both bromine atoms, yielding a substance not yet examined.

In connection with the recent sitting of the Brunswick *Naturforscherversammlung* respecting the constitution of camphor, the author concludes that it is not yet possible to definitely state the constitution of this substance. W. J. P.

Conversion of Sulphocamphophenol into Dinitrocresol. By PAUL CAZENEUVE (*Compt. rend*,, 1896, **123**, 1293—1295).—The compound previously obtained by the action of cold fuming nitric acid on the two sulphonated camphophenols and described as a tetranitroderivative, $C_9H_8O(NO_2)_4(SO_2)(OH)_2$ (Abstr., 1890, 1153), is now proved to be the dinitro-orthocresol [Me : OH : $(NO_2)_2$ = 1 : 2 : 3 : 5] previously obtained by Nevile and Winther (Trans., 1880, 631).

J. J. S.

Asymmetrical Alkylphenylhydrazines and some of their Derivatives. By C. A. AUGUST MICHAELIS (*Ber.*, 1897, **30**, 2809—2821. Compare *Ber.*, **20**, 2485).—The hydrochlorides of the asymmetrical alkylphenylhydrazines can readily be freed from phenylhydrazine hydrochloride by recrystallisation from chloroform or benzene, in which the latter is either insoluble or only sparingly soluble.

[With G. ROBISCH.]—*a-Phenylethylhydrazine*, NH_2·NEtPh.—This is best prepared by the action of ethylic iodide on sodium phenylhydrazine (Abstr., 1889, 1158). It boils at 237° (corr.) and has a sp. gr. = 1·018 at 15°. It readily reacts with pyruvic ac d to form a derivative which on heating with hydrochloric acid at 60° yields ethylindolecarboxylic acid (E. Fischer and O. Hess, *Ber.*, **17**, 565). When this acid is heated at 190—195°, carbonic anhydride is evolved and 1'-*ethylindole*, $C_6H_4<{NEt \atop CH}>CH$, produced; the latter boils at 252—253° (corr.) and has a sp. gr. = 1·2563 at 15°. Its *picrate* crystallises in red needles and melts at 105°. *Dichlorethyloxindole*, $C_6H_4<{NEt \atop CCl_2}>CO$, obtained by the action of sodium hypochlorite on ethylindolecarboxylic acid, crystallises in yellowish prisms melting

at 56°; *dibromethyloxindole* crystallises in yellow prisms melting at 95—96°. Water converts these halogen derivatives into ethyl-ψ-isatin, whilst aqueous soda yields *sodium ethyl-ψ-isatate*,

$$NHEt\cdot C_6H_4\cdot CO\cdot COONa.$$

Ethyldioxindole, $C_6H_4<\begin{matrix}-NEt-\\ CH(OH)\end{matrix}>CO$, which can readily be prepared by the reduction of ethyl-ψ-isatin, crystallises in colourless prisms which soften at 143° and melt at 154—155°. 1′-*Ethyloxindole*, $C_6H_4<\begin{matrix}NEt\\ CH_2\end{matrix}>CO$, obtained by the reduction of dibromethyloxindole, crystallises in needles and is probably identical with that prepared by Baeyer and Comstock by the ethylation of oxindole (Abstr., 1883, 1130).

a-Phenylpropylhydrazine, $NH_2\cdot NPrPh$, which boils at 247° (corr.) and has a sp. gr. = 0·9471, reduces Fehling's solution only very slowly in the cold and has an odour which resembles that of onions. 1′-*Propylindolecarboxylic acid*, $C_6H_4<\begin{matrix}NPr\\ CH\end{matrix}\geqslant C\cdot COOH$, prepared in a similar manner to the ethyl compound, crystallises in white needles which melt at 170°, and then sublime and decompose into carbonic anhydride and 1′-*propylindole*; the latter is a colourless oil, which boils at 265° (corr.) and has a sp. gr. = 1·0559 at 15°. Its *picrate* forms red needles melting at 67°. *Dichloropropyloxindole* crystallises in yellowish needles melting at 67°; the *dibromo*-derivative forms prisms melting at 97°. 1′-*Propyl-ψ-isatin* crystallises in slender, bright-red needles melting at 72°. Barium propyl-ψ-isatate, obtained by the action of baryta water on dichloropropyloxindole, crystallises in silky, yellow needles. The *β-oxime*, $C_6H_4<\begin{matrix}-NPr-\\ C(N\cdot OH)\end{matrix}>CO$, melts at 88°, and does not yield indigo when treated with ammonium sulphide. *Propyldioxindole* crystallises in yellow needles melting at 70°. *Propyloxindole* forms colourless crystals melting at 68—69°; bromine water added to its solution precipitates a bromine *compound* melting at 125°.

[With R. Ilmer.]—*Isopropylphenylhydrazine*, $NPh(CHMe)_2\cdot NH_2$, prepared in a similar manner to the ethyl compound, boils at 236° and has a sp. gr. = 0·9588 at 15°. 1′-*Isopropylindolecarboxylic acid* melts at 183°, and the corresponding *indole* boils at 250° and forms a *picrate* which melts at 76°. *Trinitrohydrazoisopropylbenzene*,

$$NPhPr\cdot NH\cdot C_6H_2(NO_2)_3,$$

formed by the action of picrylic chloride on isopropylphenylhydrazine in alcoholic solution, crystallises in brownish-red needles melting at 156°. It readily dissolves in aqueous alkalis, but no salts of it could be prepared. It is not acted on by mercuric oxide, and in this respect differs from trinitrophenylhydrazine, which is thereby converted into an azo-compound. Dinitrohydrazoisopropylbenzene,

$$NPhPr\cdot NH\cdot C_6H_3(NO_2)_2,$$

obtained by the action of chlorodinitrobenzene on the hydrazine, crystallises in brownish-red needles which are insoluble in aqueous alkalis. *a-Phenylisobutylhydrazine* boils at 245°, and has a sp. gr. = 0·9633 at 15°. 1′-*Isobutylindolecarboxylic acid* crystallises in white, silky needles melting at 152°. 1′-*Isobutylindole* boils at 260°, and does

not form a crystallisable compound with picric acid. *Trinitrohydrazoisobutylbenzene*, $C_4H_9\cdot NPh\cdot NH\cdot C_6H_2(NO_2)_3$, crystallises in red needles, melts at 105°, and dissolves in alkalis; the *dinitro*-derivative also crystallises in red needles and melts at 151°. *a-Phenylisoamylhydrazine* boils at 262°, and has a sp. gr. = 0·9680 at 15°. 1′-*Isoamylindolecarboxylic acid* melts at 122°, whilst the corresponding *indole* boils at 276° and does not form a solid picrate. *Trinitrohydrazoisoamylbenzene* forms red needles melting at 58°, whilst the *dinitro*-compound crystallises in bright yellow needles, and melts at 104°. A. H.

4′-Amidoquinoline. By Adolph Claus and Walther Frobenius (*J. pr. chem.*, 1897, **56**, 181—204. Compare Abstr., 1894, i, 617).—4′-*Amidoquinoline*, prepared by a method already described, melts at 70° after recrystallisation from the ordinary solvents; it contains $1H_2O$, which it loses at 100°, and then melts at 154°. It is easily soluble in alcohol, but less readily so in ether and benzene. The *hydrochloride* crystallises in small, colourless leaflets very readily soluble in water, and remains unchanged when heated to 300°; the *platinochloride* forms orange-coloured needles containing $2H_2O$; the *nitrate* crystallises in small needles which melt at 214° after driving off $1H_2O$; and the *dichromate* crystallises in bunches of long, orange-red needles which decompose on exposure to air or on heating to 207°. On warming the base with methylic iodide at a temperature of 50—60°, it is completely transformed into the *methiodide*, which crystallises from alcohol in colourless needles melting at 224°; the *methochloride*, prepared by treating the methiodide with silver chloride, crystallises in colourless needles melting at 310°; the *metho-dichromate* crystallises in orange-red needles, becoming brown on exposure to air, and melting at 225° with decomposition, whilst the *ethiodide* crystallises in colourless needles melting at 232°.

When 4-amidoquinoline methiodide is treated with moist silver oxide or concentrated potash, small amounts of the ammonium hydroxide base are formed, and in their behaviour towards these reagents the quaternary 4′-amidoquinoline compounds take up a position intermediate between the para- and ortho-alkoxyquinoline derivatives. (Compare Claus and Howitz, Abstr., 1891, i, 1252.)

4′-*Acetamidoquinoline*, $NHAc\cdot C_9H_6N + H_2O$, crystallises from water in colourless, glistening needles, melts at 172°, and sublimes without decomposition. The *methiodide*, formed by heating the base with methylic iodide in sealed tubes at 120°, crystallises from alcohol in yellow leaflets, becoming black on heating to 250°, and melting at 291° with decomposition.

Claus and Howitz have already shown that when 4′-amidoquinoline is treated with sodium nitrite in hydrobromic acid solution, no diazo-derivative is obtained, but only 3′-bromo-4′-amidoquinoline, and also, as is now proved, 3′-bromoquinoline melting at 29—30°.

3′-*Iodo*-4′-*amidoquinoline*, prepared in a similar manner, crystallises from water in colourless needles containing $1H_2O$ and melting at 197°.

4′-*Iodoquinoline* is obtained in small quantities when 4′-amidoquinoline is diazotised in concentrated sulphuric acid solution and the product treated with potassium iodide. It is insoluble in cold water,

readily soluble in alcohol and ether, crystallises in colourless needles or prisms melting at 97°, and sublimes without decomposition. The *platinochloride* crystallises in orange-red needles, decomposing when heated to 185° with elimination of iodine; and the *methiodide* separates from water in bunches of reddish-yellow needles which decompose when heated to 251°.

By the action of nitric acid alone, 4′-amidoquinoline does not yield a nitro-compound, but the nitro-derivative of kynurine. *Nitro-4′-amidoquinoline* may, however, be produced by gradually adding 4′-amidoquinoline sulphate to well cooled fuming nitric acid; it crystallises from water in long, yellow needles containing $1H_2O$, and decomposes when heated to 207°. In all probability, the nitro-group is in the 3′-position of the pyridine ring, as the substance is easily dissolved by alkalis; the *sodium* compound forms small, colourless needles. It is very feebly basic, for although the *hydrochloride* may be obtained as colourless needles by adding the calculated amount of hydrochloric acid to an alcoholic solution of the base, it is immediately dissociated in presence of water. The *platinochloride* forms orange-red crystals, which decompose at 210°, and are at once dissociated in presence of water. The nitro-derivative is indifferent towards alkyl halogen compounds and does not form a diazo-compound.

Dinitro-4′-amidoquinoline, prepared by treating 4′-amidoquinoline with a mixture of nitric and sulphuric acids, crystallises from dilute alcohol in golden-yellow needles which decompose suddenly when heated to 203°. It does not form salts with acids, neither does it combine with methylic iodide, or give a diazo-compound. The *platinochloride* can be obtained with difficulty, but it dissociates immediately in presence of water.

During the nitration, a second substance is formed in small amount crystallising from dilute alcohol, and decomposing at 285°. Its nature and composition will be further investigated, but it appears to be represented by one of the two formulæ $C_{18}H_{12}N_7O_7$ or $C_{18}H_{10}N_7O_7$.

A. W. C.

2′-Amidoquinoline. By ADOLPH CLAUS and S. SCHALLER (*J. pr. chem.*, 1897, **56**, 204—212. Compare preceding abstract).—*2′-Amidoquinoline* is prepared by heating 2′-chloroquinoline, ammonium carbonate and ammonium hydroxide in sealed tubes for 5—6 hours at 200—210°, and is separated from the carbostyril formed at the same time by treatment with benzene, in which the latter is insoluble. It crystallises from water in large, colourless or slightly yellow leaflets, melts at 125°, is readily soluble in ether, alcohol, and benzene, almost insoluble in chloroform and light petroleum, and sublimes readily in large, glistening, iridescent crystals; in contact with alkalis, it is converted into carbostyril. The *platinochloride* forms glistening orange-yellow crystals containing $2H_2O$; the *methiodide* crystallises from alcohol in colourless needles and from water in prismatic crystals melting at 245°, and the *methochloride* forms silken needles melting at 265°.

The methiodide differs markedly from the corresponding derivative of 4′-amidoquinoline in giving with moist silver oxide a considerable

quantity of the quaternary ammonium hydroxide base. This subject will be treated more fully in a subsequent paper. A. W. C.

Action of Aromatic Amines on Certain Unsymmetrical Ketonic Compounds. By LOUIS SIMON (*Ann. Chim. Phys.*, 1896, [vii], **19**, 433—536. Compare Abstr., 1893, i, 552; 1894, i, 509; 1895, i, 594, and 1896, i, 85).—Aniline reacts with pyruvic acid in the presence of ether, yielding three products, (1) anilpyruvic acid NPh:CMe·COOH, (2) 2′-methylquinoline-4′-carboxylic acid (aniluvitonic acid), and (3) a colourless, crystalline compound, $C_{17}H_{18}N_2O_2$, melting at 190° and having the composition

$$OH{\cdot}CHMe{\cdot}CH_2{\cdot}C(:NPh){\cdot}CO{\cdot}NHPh, \text{ or } NHPh{\cdot}CHMe{\cdot}CH_2{\cdot}C(:NPh){\cdot}COOH.$$

Other primary aromatic bases react in the same manner.

With pyruvic acid, paratoluidine yields *paratolilpyruvic acid* melting at 127°, 3 : 2′-*dimethylquinoline*-4′-*carboxylic acid* melting at 265°, and the *compound* $C_{19}H_{22}N_2O_2$, forming white crystals and melting at 238°; orthotoluidine yields *orthotolilpyruvic acid* melting at 137°, 1 : 2′-*dimethylquinoline*-4′-*carboxylic acid* melting at 252°, and the compound $C_{19}H_{22}N_2O_2$ melting at 232°; whilst metaxylidine yields metaxylilpyruvic acid melting at 137—138°, a *trimethylquinoline*-4′-*carboxylic acid* [?Me_3 = 1 : 3 : 2′] melting at 212°, and the *compound* $C_{21}H_{26}N_2O_2$ melting at 232°.

β-Naphthylamine in like manner gives *β-naphthilpyruvic acid* melting at 132°, a compound melting at 232°, and as Doebner and others have already shown, β-naphthyluvitonic acid.

The compounds with aniline have already been prepared by Boettinger, who, however, ascribed somewhat different constitutions to them. The products formed from aniline and the ethereal salts of pyruvic acid have already been described (Abstr., 1896, i, 85). α-Naphthylamine does not react with pyruvic acid. J. J. S.

Ethylic Phenacetylmalonate. By HERMANN METZNER (*Annalen*, 1897, **298**, 374—390. Compare Schott, Abstr., 1896, i, 700).—Ethylic phenacetylmalonate is converted into benzyl methyl ketone when heated with hydrochloric acid (sp. gr. = 1·1) for several hours; alcoholic potash resolves it into phenylacetic acid. Concentrated aqueous ammonia gives rise to phenylacetamide and malonamide, and aniline, which acts less rapidly, converts it into phenylacetanilide.

Ethylic benzylisoxazolonecarboxylate, $O\!<\!\begin{matrix}N{=\!=}C{\cdot}CH_2Ph\\ CO{\cdot}CH{\cdot}COOEt\end{matrix}$, is prepared by heating ethylic phenacetylmalonate dissolved in 60 per cent. alcohol with hydroxylamine hydrochloride and sodium carbonate on the water bath; it softens at 124°, and melts at 143°. The alcoholic solution gives a deep red coloration with ferric chloride, but does not reduce boiling Fehling's solution. The *silver* derivative is white, and the *aniline* compound melts and decomposes at 160°.

On heating ethylic phenacetylmalonate with phenylhydrazine, Schott obtained ethylic 1 : 5 : 3-phenylbenzylpyrazolone-4-carboxylate (*loc. cit.*); if, however, the salt is heated with a solution of the base in glacial acetic acid, 1 : 5 : 3-*phenylbenzylpyrazolone*,

$$N\lt\begin{matrix}NHPh\cdot C\cdot CH_2Ph \\ CO\text{——}CH\end{matrix},$$

is produced, and crystallises in plates melting at 131—134°. It develops a deep red coloration with ferric chloride, but does not give Bülow's reaction for hydrazides.

Ethylic 1 : 3-*dihydroxynaphthalene-2-carboxylate* is obtained by dissolving ethylic phenacetylmalonate in concentrated sulphuric acid, and pouring the liquid into cold water; it crystallises from dilute alcohol or acetic acid in yellowish needles, and melts at 83—84°. The alcoholic solution gives a blue coloration with ferric chloride. The *diacetyl* derivative crystallises in slender, white needles, and melts at 64°. The *diamine*, which is produced in small quantity when the substance is heated with aqueous ammonia at 100°, melts at 168—172°, and its solution becomes coloured in consequence of oxidation. The *monanilide* derivative crystallises from acetic acid in rhombic plates, and melts at 185°. The *dibromo*-derivative crystallises in yellow needles, and melts at 159—160°; the alcoholic solution gives a blue coloration with ferric chloride.

1 : 3-*Dihydroxynaphthalene-2-carboxylic acid* is prepared from the ethylic salt by heating it with aqueous baryta at 80°, hydrogen being passed through the solution during the operation; it crystallises from water in clusters of yellowish needles, and melts at 145°, when it evolves carbonic anhydride. The *silver* salt has been analysed. When the acid is boiled with water, it is converted into 1 : 3-dihydroxynaphthalene (Friedländer and Rüdt, Abstr., 1896, i, 569).

M. O. F.

Salts of Phenylphenazonium and Phenylnaphthophenazonium and their Reaction with Alkalis and Amines. By FRIEDRICH KEHRMANN and W. SCHAPOSCHNIKOFF (*Ber.*, 1897, 2620—2628. Compare Abstr., 1897, i, 172).—*Phenylphenazonium dichromate*, $(C_{18}H_{13}N_2)_2Cr_2O_7$, forms small, ochre-yellow prisms; the *platinochloride* is a sparingly soluble, brownish-yellow, crystalline powder, and the *aurochloride* a heavy, ochre-yellow precipitate; the *chloride* has only been obtained in solution; the *iodide* is a brown, crystalline precipitate, and the *mercurochloride* and *picrate* are also crystalline precipitates. Phenylphenazonium ferric chloride is converted by aqueous soda into aposafranone, $C_{18}H_{12}N_2O$, identical with the product obtained by Jaubert (Abstr., 1895, i, 219). Alcoholic ammonia converts phenylphenazonium ferric chloride into aposafranine chloride,

$$NH_2\cdot C_6H_3\lll\begin{matrix}N\text{——} \\ NPhCl\end{matrix}\ggg C_6H_4.$$

The hydro-derivative of the phenazonium compound, $C_6H_4\lt\begin{matrix}NH \\ NPh\end{matrix}\gt C_6H_4$, is also formed, but is rapidly oxidised by the oxygen of the air, and is thus reconverted into the original phenazonium derivative, which then again reacts with the ammonia, all the original substance being finally converted into aposafranine, or decomposed by secondary reactions.

Dimethylaposafranine nitrate, $NMe_2\cdot C_6H_3\lll\begin{matrix}N\text{———} \\ NPh(NO_3)\end{matrix}\ggg C_6H_4$, obtained by acting on the phenylphenazonium ferric chloride with

dimethylamine and precipitating with sodium nitrate, crystallises with $\frac{1}{2}H_2O$ in thick prisms with a bronze lustre. The *platinochloride* forms lustrous granules, and the *dichromate* a brownish-violet, crystalline powder. The salts give bluish-green solutions in sulphuric acid, which become violet on the addition of water. Aniline converts the phenylphenazonium ferric chloride into the phenylaposafranine chloride previously obtained by Fischer and Hepp (Abstr., 1897, i, 636). This is accompanied by *anilidophenylaposafranine chloride*,

$$C_6H_4<\genfrac{}{}{0pt}{}{N}{NPhCl}>C_6H_2(NHPh)_2,$$

which crystallises in granules with a green, metallic lustre. The salts of phenylnaphthophenazonium are converted by concentrated soda into rosindone, $O<\genfrac{}{}{0pt}{}{C_{10}H_5:N}{NPh-C_6H_4}$, and by ammonia into rosinduline chloride, $C_6H_4<\genfrac{}{}{0pt}{}{N}{NPhCl}>C_{10}H_5\cdot NH_2$. Dimethylamine produces salts of dimethylrosinduline, which readily decompose in alkaline solution with formation of rosindone and dimethylamine. The *nitrate*,

$$NMe_2\cdot C_{10}H_5<\genfrac{}{}{0pt}{}{N}{NPh(NO)_3}>C_6H_4,$$

crystallises with $\frac{1}{2}H_2O$ in prisms with a greenish lustre. The *platinochloride* and *dichromate* are sparingly soluble, crystalline precipitates.

A. H.

Salts of Phenylisonaphthophenazonium and the Action of Amines on them. By FREDERICH KEHRMANN and WILHELM HELWIG (*Ber.*, 1897, **30**, 2629—2636. Compare Abstr., 1897, i, 107, 172).—*Phenylisonaphthophenazonium hydroxide*, $C_{10}H_6<\genfrac{}{}{0pt}{}{N}{NPh(OH)}>C_6H_4$, is formed, together with a small amount of phenylnaphthophenazonium hydroxide, by the condensation of β-naphthaquinone with amidodiphenylamine. Some of its salts have already been described. The double ferric chloride crystallises in lustrous, orange-yellow plates melting at 200·5°; the *nitrate* forms reddish-yellow, compact crystals, which melt and decompose at 229°; the *platinochloride* is an orange-red, crystalline powder; the aurochloride melts at 240°, and the dichromate is a scarlet-red powder. The salts of phenylisonaphthophenazonium are converted into amido-derivatives by alcoholic ammonia. 3-*Amidophenylisonaphthophenazonium chloride* (isorosinduline chloride, No. 4),

$$C_{10}H_6<\genfrac{}{}{0pt}{}{NPhCl}{N}>C_6H_4\cdot NH_2,$$

crystallises in violet-red needles which dissolve in water, forming a magenta-red solution, from which aqueous soda precipitates the free base; the *platinochloride* crystallises in violet needles, and the *nitrate* in flat prisms with a coppery lustre. 3-*Dimethylamidophenylisonaphthophenazonium nitrate* (dimethylisorosinduline nitrate), $C_{24}H_{20}N_3\cdot NO_3$, is obtained by the action of dimethylamine on the isonaphthophenazonium salts. It crystallises in indigo-blue prisms with a coppery lustre, and melts with decomposition at 220°. The *aurochloride* forms blue crystals which melt and decompose at 200—203°; the *platinochloride* also forms blue crystals. 3-*Phenylamidophenylisonaphthophenazonium*

chloride (phenylisorosinduline chloride), prepared by heating the double ferric chloride with aniline, is a heavy, crystalline powder almost insoluble in cold water; its *platinochloride* is an insoluble, blue, crystalline precipitate.

The position of the amido-group in these derivatives has not been definitely ascertained, but from the analogy of the phenylnaphthophenazonium compounds it is probable that it takes up the para-position relatively to the azine nitrogen atom. A. H.

The Fifth Isomeride of Rosinduline. By FRIEDRICH KEHRMANN and O. FEDER (*Ber.*, 1897, 30, 2637—2641).—*Nitrorosinduline chloride*, $\overset{4}{N}H_2\cdot C_{10}\overset{1,2}{H_5}\lessdot\genfrac{}{}{0pt}{}{N\text{——}}{NPhCl}\!>\overset{1,2}{C_6}H_3\cdot\overset{4}{N}O_2$, obtained by heating nitramidodiphenylamine hydrochloride with oxynaphthaquinonimide in alcoholic solution (Rademacher, These, Berlin), is a heavy, dark red, crystalline powder with a greenish lustre. A number of derivatives of this compound have been prepared and will be described by Rademacher in another communication. When this substance, in acid solution, is treated with sodium nitrite, and then with alcohol, hydrogen is substituted for the amido-group, and salts of 4-nitrophenylnaphthophenazonium are formed. The *double ferric chloride*,

$$C_{22}H_{14}N_3O_2Cl + FeCl_3,$$

is a reddish-brown, sandy, crystalline powder. The *nitrate* forms green, metallic looking-needles. The aqueous solutions of both this and the other salts decomposes when warmed, nitrorosindone being deposited. The *chloride* crystallises with $2H_2O$ in green needles; the *platinochloride*, *aurochloride*, and *dichromate* are insoluble crystalline precipitates.

The nitro-compound can readily be converted by reduction into the corresponding amido-derivative, *isorosinduline chloride* (No. 5), $C_{10}H_6\lessdot\genfrac{}{}{0pt}{}{N\text{——}}{NPhCl}\!>C_6H_5\cdot NH_2$, which crystallises in long, lustrous, black-violet needles, and is readily soluble in water; the *nitrate* crystallises with $1H_2O$, and is almost insoluble in dilute nitric acid; the *platinochloride* forms bluish-black, insoluble needles. A. H.

Triazine Derivatives from Chrysoidine and from Orthamidoazotoluene. By EMILIO NOELTING and F. WEGELIN (*Ber.*, 1897, 30, 2595—2604).—Diamidoazo-compounds react with benzaldehyde in a similar manner to monamido-compounds (Goldschmidt and Rosell, Abstr., 1890, 614), triazine derivatives being formed, which are capable of undergoing the diazo-reaction.

The *triazine* from chrysoidine and benzaldehyde,

$$NH_2\cdot C_6H_3<\begin{matrix}N\cdot NPh\\ | \quad\ |\\ N\cdot CHPh\end{matrix},$$

is a yellowish powder, solutions of which rapidly become brown in the air. The *sulphate* is sparingly soluble. The *acetyl* derivative is a white powder which melts at 216°; the *benzoyl* derivative melts at 221°. The triazine readily forms diazo-salts, which yield red colouring matters with β-naphthol, resorcinol, and other phenols and amido-compounds. Fuming sulphuric acid converts the triazine into a mixture of

sulphonic acids, which have an extremely sweet taste. The sulphotriazines obtained from sulphonated chrysoidines all have this sweet taste, whereas the compound from chrysoidine and benzaldehydemetasulphonic acid has a bitter taste. When the amido-group of chrysoidineparasulphonic acid is replaced by hydrogen, the salts of the resulting acid, which crystallises in needles, also have a sweet taste. These three acids are all insoluble in cold water, sparingly soluble in hot water.

The *triazine* from chrysoidine and orthonitrobenzaldehyde,

$$C_{19}H_{15}N_5O_2,$$

crystallise in yellow tablets, melts and decomposes at 118—119°, and on reduction yields an *amido*-compound, which melts and decomposes at 204°. The *triazine* from metanitrobenzaldehyde forms yellow crystals which melt and decompose at 204—205°. The *amido*-compound melts and decomposes at 187°. The *triazine* from paranitrobenzaldehyde forms red crystals which melt and decompose at 211°, and are less soluble than those of the ortho-compound. The *amido*-derivative melts at 200°. The colouring matters formed from the azo-derivatives of these three amidotriazines with amidonaphtholsulphonic acid G,$[NH_2 : OH : SO_3H = 1 : 1' : 3']$, and amidonaphtholdisulphonic acid H,$[NH_2 : OH : (SO_3H)_2 = 1 : 1' : 3 : 3']$ have also been examined. They dye cotton without mordants violet to blue, but are not fast to acids. The ortho-compounds have the least colouring power, the para-compounds the greatest.

The *triazine* from orthamidoazotoluene and orthonitrobenzaldehyde, $C_{21}H_{18}N_4O_2$, crystallises in yellow needles melting at 230°. The *triazine* from the metanitrobenzaldehyde forms yellowish needles melting at 228°, whilst that from the para-compound melts at 264°. Metahydroxybenzaldehyde yields a *triazine*, $C_{21}H_{19}N_3O$, which crystallises in white needles melting at 265°. Metasulphobenzaldehyde yields a *triazine*, $C_{21}H_{19}N_3SO_3$, which is a crystalline powder. Phthalic anhydride does not yield analogous compounds with amidoazotoluene, but simply forms an acid derivative. A. H.

Dimethylconiine. By MARTIN MUGDAN (*Annalen*, 1897, **298**, 131—147. Compare Abstr., 1894, i, 555).—It has been pointed out (*loc. cit.*) that whilst the optical activity of dimethylconiine appears to condemn the formula $CHPr\colon CH\cdot[CH_2]_3\cdot NMe_2$, its abnormal behaviour towards hydrogen chloride renders the expression

$$CH_2\colon CH\cdot CH_2\cdot CH_2\cdot CHPr\cdot NMe_2$$

equally improbable; the constitution of the base has been therefore expressed by the formula $NMe_2\cdot CH<\begin{matrix}CH_2—CH_2\\ CHPr\cdot CH_2\end{matrix}$. The author, however, finds that dimethylpentamethenylamine, $NMe_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}$, which should resemble in behaviour the higher homologues, dimethyl-α-pipecoline and dimethylconiine, differs from them greatly. Dimethylconiine, moreover, obtained by distilling dimethylconium hydroxide, can be resolved into three fractions which exhibit marked differences in optical activity, and from a study of the behaviour of crude dimethylconiine towards hydrogen iodide, it appears that

methylconiine is present in the base. In addition to this substance, the crude base consists of two isomeric dimethylconiines, yielding the two corresponding dihydrodimethylconiines on reduction; one of these products has been identified as normal dimethyloctylamine.

It is shown, therefore, that when dimethylconium hydroxide is submitted to distillation, change proceeds in three directions. In the first place, methylic alcohol is eliminated, giving rise to a small quantity of methylconiine; when, however, water is separated, scission occurs between nitrogen and the 2-carbon atom on the one hand, giving rise to dimethylconiine of the formula $CH_2{:}CH\cdot CH_2\cdot CH_2\cdot CHPr\cdot NMe_2$, whilst on the other hand the base of the formula $CHPr{:}CH\cdot[CH_2]_3\cdot NMe_2$ is produced when scission occurs between nitrogen and the 6-carbon atom.

Dimethylpentamethenylamine, $NMe_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}|$, is prepared from pentamethenylamine by the action of methylic iodide, and conversion of the substituted ammonium iodide into the ammonium chloride, which is then distilled at 330°; it is a colourless base having the odour of trimethylamine, and boils at 133·5—135°. Unlike pentamethenylamine, it is scarcely soluble in water; the *hydrochloride* crystallises from acetone in colourless, hygroscopic leaflets. Both the original base and the dimethyl derivative are coloured by one drop of an alcoholic solution of iodine, whilst the latter is immediately decolorised by dimethylconiine. Dry dimethylpentamethenylamine hydrochloride absorbs hydrogen chloride, which causes it to liquefy, but the halogen is completely removed by water, which is not the case with hydrochlorodimethylconiine hydrochloride. The aurochlorides of dimethylpiperidine, dimethylpipecoline, and dimethylconiine, moreover, differ from the aurochloride of dimethylpentamethenylamine in their unstable character, the solution of the last-named salt undergoing no change when boiled.

When dry hydrogen iodide is passed into dimethylconiine, it is found that, in addition to methylconiine, the base consists of a mixture of two isomerides; the *hydriodide* of one crystallises in short prisms and melts at 220°, whilst the *hydriodide* of the other, which is produced in four times the amount, is more readily soluble in a mixture of alcohol and ethylic acetate, from which it crystallises in thick needles and melts at 151—152°. A 10 per cent. solution of the former salt has $a = 5·2°$, whilst the hydriodide of lower melting point has $a = 0·36°$. The derivatives of the latter salt closely resemble those of dimethylconium iodide, and the chloride on distillation yields a base which boils at 173·5—177°, and has the odour and formula of methylconiine.

Dimethyldihydroconiine, $C_{10}H_{23}N$, obtained by reducing the product of the action of hydrogen iodide on dimethylconiine, with zinc dust and glacial acetic acid, has the odour of the base from which it is derived; it boils at 184—186°, has the sp. gr. = 0·7795 at 14°/4°, the refractive index $n_D = 1·4288$, and the rotation angle $a = 3·6°$ in a 1 decimetre tube. The *aurochloride* crystallises in elongated leaflets, and is stable in solution; the *platinochloride* melts at 117°. Methylic iodide gives rise to a mixture which melts at 166°, and consists of the

methiodide which melts at 139—141°, and the somewhat more readily soluble *methiodide* melting at 190°; the former of these has been identified with trimethyloctylammonium iodide which melts at 139—141°, whilst the *platinochloride* and *aurochloride* melt at 240°, and 91—93° respectively. M. O. F.

Derivatives of Theobromine. Action of Chloroform on Phenylhydrazine. By HEINRICH BRUNNER and HEINRICH LEINS (*Ber.*, 1897, **30**, 2584—2587).—The *propyl*, *isopropyl*, *butyl*, and *amyl* derivatives of theobromine were obtained by heating silver theobromine with the corresponding iodide. All these substances form crystalline granules melting above 270°.

Van der Slooten (Abstr., 1897, i, 382) has prepared a series of alkyltheobromines by the action of alkyl iodides on an alcoholic solution of potassium theobromine, and in this way has obtained compounds of comparatively low melting point, ,which differ from those just described. *Nitro-theobromine* $NO_2\cdot C_7H_7N_4O_2$, obtained by the direct action of nitric acid on theobromine, forms a pale yellow, microcrystalline powder, which can be sublimed. The corresponding *amido*-compound is sparingly soluble in alcohol and can also be sublimed.

When chloroform is heated or allowed to stand with phenylhydrazine, the hydrochloride of the latter is produced. No carbophenylhydrazine appears to be formed. A. H.

New Decomposition of Theobromine. By EMIL FISCHER and FRITZ FRANK (*Ber.*, 1897, **30**, 2604—2618).—When theobromine is suspended in chloroform and treated with chlorine, it is converted into an unstable substance rich in chlorine which separates in crystals but decomposes even in dry air. Its composition has not been ascertained. When this substance is treated with water it yields *theobromuric acid*, $COOH\cdot NH\cdot CO\cdot NMe\cdot C\begin{matrix}\diagup CO\cdot NMe \\ \diagdown N—CO\end{matrix}$, which crystallises from lukewarm water in small, colourless needles or prisms, melts with evolution of gas at about 181° (corr.), and does not reduce ammoniacal silver oxide or give the murexide reaction. It readily undergoes etherification, yielding ethereal salts, which are also formed by the action of alcohols on the chlorine derivative; the *ethylic* salt forms compact, colourless prisms terminated by pyramids, and melts at 212° (corr.); the *methylic* salt also crystallises well and melts at 199—200° (corr.). Hot water decomposes theobromuric acid with evolution of carbonic anhydride and formation of the *methylcarbamide salt of methylparabanic acid*; this melts at 127—128° (corr.), decomposes at about 195°, and is converted by alkalis into methylcarbamide and oxalic acid, whilst hydrochloric acid decomposes it with formation of the carbamide and methylparabanic acid. It can readily be obtained by the union of its constituents, and is also formed when methylcarbamide is heated with ethylic oxalate at 100°; this reaction affords a new synthesis of methylparabanic acid. The constitution of theobromuric acid has not been definitely ascertained.

Hydriodic acid converts both the free acid and its ethereal salts into

the *anhydride of hydrotheobromuric acid*, $C_7H_8N_4O_4$, which crystallises in long, colourless needles and melts and decomposes at 264° (corr.); it dissolves in alkalis, forming salts of *hydrotheobromuric acid*, $C_7H_{10}N_4O_5$, which separates when these solutions are acidified, and crystallises with $1H_2O$ in long, colourless, matted needles. The acid becomes anhydrous at 110° and then melts and decomposes at 231° (corr.). It is reconverted by 20 per cent. hydrochloric acid into the anhydride. The *ethylic* salt crystallises in matted needles melting at 206—207° (corr.). Dilute baryta water converts hydrotheobromuric acid into carbonic anhydride, methylamine, and *theuric acid*, $C_5H_7N_3O_4$; the latter is readily soluble in hot water, crystallises in rhombic prisms, melts and decomposes at about 254° (corr.). It reduces ammoniacal silver oxide and is decomposed by excess of alkali; the constitution of the acid has not been ascertained.

When ethylic theobromurate is dissolved in concentrated hydrochloric acid, a compound is formed which dissolves in water, with evolution of gas and formation of *carbonyldimethylcarbamide*, $CO(NH{\cdot}CO{\cdot}NHMe)_2$. This substance, which can be obtained by the action of phosgene on dimethylcarbamide, is a granular, crystalline powder melting at 199—200° (corr.). It is not precipitated from a warm aqueous solution by mercuric nitrate, and gives no coloration with copper sulphate in alkaline solution; these two reactions distinguish it from carbonyldicarbamide. It dissolves without change in cold dilute aqueous alkalis, but on boiling is decomposed with formation of methylcyanuric acid.

Nitrous acid converts it into *nitrosocarbonyldimethylcarbamide*, $C_5H_9N_4O_3{\cdot}NO$, which is a yellow, flocculent precipitate that cannot be recrystallised, and is decomposed by hot water with formation of methylcyanuric acid and methylbiuret. *Methylcyanuric acid*, $C_4H_5N_3O_3$, crystallises with $1H_2O$ in thin plates, and when dry melts at 296—297° (corr.); it sublimes readily and can be distilled in small quantities, yielding a very penetrating vapour. When treated with aqueous potash and methylic iodide, it is converted into trimethylic isocyanurate. *Methylbiuret*, $C_3H_7N_3O_2$, crystallises in prisms, melts at 165—166° (corr.) and yields a reddish-violet coloration with a dilute alkaline solution of copper sulphate. The *nitroso*-derivative is an almost colourless powder, which melts and decomposes at about 135°.

A. H.

Ketones of the Tropine Group. VIII. Constitution of Tropine. By RICHARD WILLSTÄTTER (*Ber.*, 1897, 30, 2679—2719. Compare Abstr., 1897, i, 304, and 1896, i, 655, 707).—The fact that condensation of tropinone with benzaldehyde gives rise to a dibenzylidene derivative (Abstr., 1897, i, 304), has led the author to reconsider the evidence which supports Merling's formula for tropine, with the result that it now appears necessary to submit this expression to very considerable modification.

In 1891, Merling first represented the constitution of tropine by the formula

$$CH\left\langle\begin{array}{l} CH_2 \text{——} CH_2 \\ CH(OH){\cdot}CH_2 \\ CH_2 \text{——} NMe \end{array}\right\rangle CH, \quad \text{or} \quad CH\left\langle\begin{array}{l} CH_2 \text{——} CH_2 \\ CH_2{\cdot}CH(OH) \\ CH_2 \text{——} NMe \end{array}\right\rangle CH,$$

the position of the hydroxylic group being uncertain; accordingly, tropinone, the ketone obtained by oxidising tropine with chromic anhydride, was regarded by Willstätter as having the structure

$$CH\left\langle\begin{array}{l}CH_2\cdot CH_2\\ CO-CH_2\\ CH_2\cdot NMe\end{array}\right\rangle CH$$

(Abstr., 1896, i, 327). It was to be expected from the behaviour of camphor and menthone towards benzaldehyde in presence of hydrogen chloride, that tropinone would yield a benzylidene derivative analogous to benzylidenecamphor and benzylidenementhone; as already stated, however, the product is dibenzylidenetropinone, and this circumstance is regarded by the author as indicating the presence of the group $-CH_2\cdot CO\cdot CH_2-$ in the ketone.

In addition to the behaviour of tropinone towards aldehydes, support is lent to this view by the action of ethylic oxalate, amylic nitrite, and diazobenzene chloride. It is known that the introduction of acidic radicles into ketones by means of sodium ethoxide affords a method of determining the number of methylenic groups in immediate connection with carbonyl, acetone, for instance, first yielding ethylic acetoneoxalate, $COMe\cdot CH_2\cdot CO\cdot COOEt$, and then ethylic xanthochelidonate, $CO(CH_2\cdot CO\cdot COOEt)_2$; similarly, tropinone is converted by ethylic oxalate and sodium ethoxide, first into ethylic tropinoneoxalate, $C_8H_{12}NO\cdot CO\cdot COOEt$, and subsequently into ethylic tropinonedioxalate, $C_8H_{11}NO(CO\cdot COOEt)_2$. Again, when amylic nitrite acts on tropinone under the influence of hydrogen chloride dissolved in glacial acetic acid, di-isonitrosotropinone, $C_8H_{11}N_3O_3$, is produced, affording strong evidence of the presence of two methylenic groups attached to carbonyl; the compound produced in this manner may be regarded as the 1 : 3-dioxime of *tropanetrione*, the 1 : 2 : 3-triketone of the tropine series. Furthermore, diazobenzene in acetic acid solution converts tropinone into the compound $C_{20}H_{21}N_5O$, which constitutes the 1 : 3-diphenylhydrazone of tropanetrione.

In the author's estimation, these observations establish the existence of the group, $\vdots C\cdot CH_2\cdot CO\cdot CH_2\cdot C\vdots$, in tropinone, the corresponding alcohol complex, $\vdots C\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot C\vdots$, being present in the two isomeric bases tropine and ψ-tropine. There are only three formulæ for tropine which fulfil this condition, namely,

$$\begin{array}{lll}CH_2- & CH- & CH_2\\ | & CH_2 & CH\cdot OH,\\ NMe- & CH- & CH_2\end{array}$$

$$\begin{array}{lll}CH_2- & CH- & CH_2\\ | & NMe & CH\cdot OH,\\ CH_2- & CH- & CH_2\end{array} \quad \text{and} \quad NMe\left\langle\begin{array}{ll}CH- & CH_2\\ CH_2 & CH\cdot OH,\\ CH- & CH_2\end{array}\right.$$

all of which admit of the presence of the complex, $\vdots C\cdot NMe\cdot CH(CH_2R)\cdot$, in tropidine. The third expression is excluded, however, because it does not account for the production of dihydrobenzaldehyde from tropinone methiodide and sodium carbonate (Willstätter, Abstr., 1896, i, 327); nor does it agree with the formation of normal adipic acid on oxidation of tropilene (Ciamician and Silber, Abstr., 1896, i, 397), and by treatment of methylic tropinate methiodide with potash (Willstätter, Abstr., 1896, i, 266). The latter consideration leads the author to abandon also the second of the above formulæ, and he therefore expresses tropine and

tropinone by the formulæ

$$\begin{array}{l} CH_2-CH-CH_2 \\ |\quad\quad CH_2\ \ CH\cdot OH, \\ NMe-CH-CH_2 \end{array} \quad \text{and} \quad \begin{array}{l} CH_2-CH-CH_2 \\ |\quad\quad CH_2\ \ CO \\ NMe-CH-CH_2 \end{array}$$

respectively.

According to this view, *tropan*, the name by which the author distinguishes hydrotropidine, $\begin{array}{l} CH_2-CH-CH_2 \\ |\quad\quad CH_2\ \ CH_2 \\ NMe-CH-CH_2 \end{array}$, is a cyclic combination of *n*-methylpyrrolidine with hexahydrobenzene, the periphery of the ring being composed of 6 carbon atoms and 1 atom of nitrogen; and as the two constituent members of the combination have 3 carbon atoms in common, tropine must be looked on as a hexahydrophenol in which the meta-substituents are linked. From this conception of the structure of tropine, there follow the alternative formulæ,

$$\begin{array}{l} \quad\quad CH_2\cdot CH - CO \\ \quad\quad |\quad\quad CH_2 \quad | \\ COOH\cdot CH_2\cdot CH-NHMe\cdot O \end{array}, \quad \text{or} \quad COOH\cdot CH_2\cdot CH{<}\begin{array}{l} CH_2\cdot CH\cdot COO \\ CH_2\cdot NHMe-| \end{array}$$

$$\text{and} \quad \begin{array}{l} CH_2-CH-CH \\ |\quad\quad CH_2\ \ CH \\ NMe-CH-CH_2 \end{array}, \quad \text{or} \quad \begin{array}{l} CH_2-CH-CH_2 \\ |\quad\quad CH_2\ \ CH \\ NMe-CH-CH \end{array},$$

for tropinic acid and tropidine respectively, the former in each case being the one which the author regards as the more probable.

Tropinic acid and tropidine being, as it were, the points of contact of the atropine and cocaine groups, it follows that ecgonine and anhydroecgonine are likewise derivatives of tropan, and the formulæ for these substances put forward by Einhorn and Tahara (Abstr., 1893, i, 377) will therefore require modification in this direction.

The modified view of the structure of tropine emphasises the analogy between the bases of this series and those derived from the rind of pomegranate root. It also becomes clear that the *n*-methylpyrrolidine ring is common to all the alkaloids of the atropine and cocaine groups (compare Liebermann and Cybulski, Abstr., 1895, i, 310).

Di-isonitrosotropinone, $\begin{array}{l} CH_2-CH-C{:}NOH \\ |\quad\quad CH_2\quad CO \\ NMe-CH-C{:}NOH \end{array}$, is prepared in the form of hydrochloride by dissolving tropinone (20 grams) in amylic nitrite (40 grams), and treating the cooled solution with glacial acetic acid (120 grams) previously saturated with hydrogen chloride at 0°; the hydrochloride which separates is washed with acetic acid and with alcohol, and treated in aqueous solution with sodium acetate, or with caustic soda followed by acetic acid. Di-isonitrosotropinone crystallises from water in bright yellow, transparent prisms, and decomposes with slight explosion at 197°; it is both basic and acidic, the aqueous solution reddening litmus. It does not give Liebermann's reaction, and develops a reddish-brown coloration with ferric chloride, whilst ferrous sulphate colours the aqueous solution an intense green; alkaline and acid solutions of potassium permanganate are immediately decolorised by

the substance, which does not, however, reduce Fehling's solution. Alkali hypochlorites readily oxidise the nitroso-compound, the yellow colour of the solution in alkalis being completely destroyed; oxidation with nitric acid gives rise to a pyrroline derivative. The *hydrochloride*, prepared in the manner described, crystallises from water in lustrous, rhombohedral plates; it becomes brown at 200° and decomposes with explosion at 260°. The *hydrobromide*, which crystallises from water in bright yellow, lustrous prisms, becomes brown at 200° and explodes at 253°. The *mono-silver* derivative forms minute needles, is insoluble in water, resists the action of light, and explodes when heated; the *silver* derivative is dark-brown and crystalline. The *dibenzoyl* derivative crystallises from dilute acetic acid in slender, long needles, and melts and decomposes at 172°; when boiled with caustic soda, it yields ammonia, hydrogen cyanide, and pyrroline bases, and it is also decomposed by boiling glacial acetic acid.

The *anhydride* of di-isonitrosotropinoneoxime (tri-isonitrosotropan), $\begin{array}{l} C_5H_9N-C{:}N \\ \mid \qquad\quad \mid \\ C(NOH)\cdot C{:}N \end{array}\!\!>O$, is obtained by heating a solution of di-isonitrosotropinone in alkali with excess of an alkaline solution of hydroxylamine, and then acidifying with glacial acetic acid; the furazan crystallises from alcohol in long, silky needles, and explodes at 185—186°. The aqueous solution gives a brown coloration with ferric chloride. The *hydrochloride* crystallises from water in six-sided plates, and decomposes vigorously at about 220°; the *benzoyl* derivative crystallises from alcohol in small, lustrous needles, and melts at 150—152°.

The action of phenylhydrazine on di-isonotrosotropinone is somewhat complicated, and gives rise to two substances. The *compound* $C_{28}H_{36}N_{10}O_5$, obtained from the free nitroso-compound, crystallises in reddish-yellow, six-sided plates, and melts at 177—178°; the *compound*, $C_{28}H_{33}N_9O_4$ arises from di-isonitrosotropinone hydrochloride, and crystallises in orange-red leaflets which melt and decompose at 224—225°.

Tribromacetoxytropinone, $C_8H_9NOBr_3\cdot OAc$, is prepared by digesting a solution of tetrabromotropinone (Abstr., 1896, i, 709) in warm glacial acetic acid with silver acetate, the liquid being filtered after an interval and diluted with water; it crystallises from alcohol in short, highly refractive prisms, if deposited slowly in quadratic plates, and melts at 148°.

Tropantrione *diphenylhyrazone*, $C_{20}H_{21}N_5O$, is prepared by adding diazobenzene chloride to a solution of tropinone in dilute acetic acid and maintaining the temperature of the liquid at 0° during 3 hours; the acetate separates when the solution is allowed to evaporate spontaneously, and on decomposing this salt with caustic soda the diphenylhydrazone is obtained. It crystallises from absolute alcohol in rosette-like aggregates of dark-red, microscopic needles, and melts and decomposes at 130°; it separates in long, slender needles containing chloroform of crystallisation when the acetate is boiled with a mixture of chloroform and absolute alcohol. The diphenylhydrazone is a colouring matter, dyeing wool an orange-red; the solution in concentrated sulphuric acid is bluish-violet and in hydrochloric acid reddish-

violet, both liquids becoming red on dilution with water (compare von Pechmann and Jenisch, Abstr., 1892, 161).

Ethylic tropinoneoxalate, $C_6H_{11}N<\begin{array}{l}CH\cdot CO\cdot COOEt\\ \vert\\ CO\end{array}$, prepared from tropinone and ethylic oxalate (1 mol.) under the influence of sodium ethoxide (2 mols.), crystallises from absolute alcohol in colourless, highly refractive, six-sided plates and melts at 169·5°, when it decomposes; the aqueous solution gives a deep cherry-red coloration with ferric chloride, and when boiled with acetic acid and sodium acetate yields a brown solution. The *platinochloride* forms red, microscopic leaflets containing $3H_2O$, and melts and decomposes at 194—195°; it is scarcely soluble in cold water, and is decomposed by the boiling liquid, giving rise to tropinone platinochloride. The *hydrochloride* of tropinoneoxalic acid is produced on boiling the ethylic salt with concentrated hydrochloric acid, and crystallises from alcohol in stellate aggregates of lustrous prisms; it melts and decomposes at 194°, and gives a deep cherry red coloration with ferric chloride.

Isonitrosotropinoneoxalic acid, $\begin{array}{l}C_5H_9N—CH\cdot CO\cdot COOH\\ \vert \qquad\quad\ \vert\\ C(NOH)\cdot CO\end{array}$, is obtained by dissolving ethylic tropinoneoxalate with amylic nitrite (1 mol.) in glacial acetic acid, and treating the solution with glacial acetic acid saturated at 0° with hydrogen chloride; the product separates in bright yellow needles and prisms, but is very unstable. Ferric chloride develops a brown coloration, and the solution in alkalis is intense yellow.

Ethylic tropinonedioxalate, $C_8H_{11}NO(CO\cdot COOEt)_2$, is prepared by dissolving ethylic tropinoneoxalate in ethylic oxalate (2 mols.), and adding sodium ethoxide (2 mols.), free from alcohol, to the solution; after some hours, the liquid is treated with water, agitated with ether, and the aqueous portion removed and acidified with acetic acid. The salt crystallises from alcohol in yellow, transparent prisms, separating from methylic alcohol in yellow, pleochromatic plates; it melts and decomposes at 176°.

Difurfurylidenetropinone, $C_8H_{11}NO(C_5H_4O)_2$, is prepared by cautiously adding a solution of tropinone (1 mol.) and furfuraldehyde (2 mols.) in ether to the same medium containing sodium ethoxide (2 mols.) in suspension; it crystallises from absolute alcohol in canary-yellow prisms, and melts at 138°. The solution in concentrated sulphuric acid is of an intense violet-red, becoming yellow on dilution with water, which precipitates the *sulphate* in slender, lustrous needles; it decolorises bromine and an acid solution of potassium permanganate. It differs from dibenzylidenetropinone in its property of dyeing wool greenish-yellow. The *hydrochloride*, which crystallises in aggregates of microscopic prisms, melts and decomposes at 237—238°; the *methiodide* crystallises from water in yellow, pleochromatic plates, and melts at 281°, when it decomposes.

Although dibenzylidenetropinone was prepared in the first instance from tropinone and benzaldehyde under the influence of hydrochloric acid, caustic soda may be also employed as the condensing agent. If, however, sodium ethoxide is used, the dibenzylidenetropinone is obtained

mixed with the *compound* $C_{22}H_{23}NO_2$, arising from condensation of tropinone with benzaldehyde (2 mols.) involving the elimination of only $1H_2O$; it contains $\frac{1}{2}H_2O$, which is removed at 70°, and it melts and decomposes at 115°. The solution in concentrated hydrochloric acid is deep red, and remains cherry-red on dilution. The *methiodide* crystallises from alcohol in prisms, and melts at 186—187°, when it decomposes.

M. O. F.

Harmine and Harmaline. By OTTO FISCHER (*Ber.*, 1897, **28**, 2481—2489. Compare Abstr., 1885, 821, and 1889, 730).—Harmaline has been shown to be dihydroharmine; both it and harmine are optically inactive in acetic acid solution. The oxidation of harmaline, $C_{13}H_{14}N_2O$, to harmine, $C_{13}H_{12}N_2O$, is best effected with potassium permanganate in dilute sulphuric acid solution. Methylharmine melts at 209°; its *hydrochloride* and flesh-coloured *platinochloride*, $(C_{13}H_{11}MeN_2O)_2,H_2PtCl_6 + 2H_2O$, were prepared; it unites with more methylic iodide, yielding a quaternary *iodide*, $C_{13}H_{11}MeN_2O,MeI$, which reacts with silver nitrate, forming the crystalline *nitrate*; the *platinochloride* and *aurochloride* of this quaternary base were also prepared. *Acetylharmaline*, $C_{13}H_{13}AcN_2O$, can be prepared by dissolving harmaline and fused sodium acetate in acetic anhydride, heating cautiously to 60°, and then setting it aside; it melts at 204—205°. *Methylharmaline*, prepared from harmaline methiodide by boiling it with baryta water, melts and decomposes at 162°, and will unite with more methylic iodide. Dihydroharmaline is best prepared by reducing harmaline with sodium in boiling amyl-alcoholic solution; its *acetyl* and *benzoyl* derivatives, $C_{13}H_{15}AcN_2O$, &c., melt at 239° and 158—159° respectively. Harmine and harmaline are oxidised to harminic acid, $C_{10}H_8N_2O_4$, by chromic acid in boiling acetic acid solution, or by nitric acid, the same product being obtained when harmol, dichloroharmine, or nitroharmine is oxidised. This acid reacts with normal alkali like a monobasic acid, but with resorcinol, like a dibasic acid, forming a fluorescein. It reacts with methylic iodide and aqueous potash, yielding *methylharminic acid*, $C_{10}H_7MeN_2O_4$, which can also be obtained by the oxidation of methylharmine, and which blackens between 260° and 280° when heated; with ethylic iodide, it yields *ethylharminic acid*, $C_{10}H_7EtN_2O_4$, which blackens at 280°. Apoharmine, formed from harminic acid by the loss of 2 mols. of carbonic anhydride, yields a yellow *picrate* melting at 247°; boiling concentrated nitric acid converts it into a derivative, $C_8H_7(NO_2)N_2$, which melts and decomposes at 270°, and is soluble in alkalis; with methylic iodide, it yields the hydriodide of *methylapoharmine*, $C_8H_7MeN_2$, which base melts at 77—78°, and yields a yellow *platinochloride* which decomposes at 260°.

C. F. B.

Organic Chemistry.

The Number of Isomeric Paraffins. By SIMA M. LOSANITSCH (*Ber.*, 1897, 30, 3059—3060. Compare this vol., i, 1).—A reply to Hermann (this vol., i, 101). The author is still of opinion that the number of possible isomeric hydrocarbons, $C_{12}H_{26}$, is 354, and not 355.

J. J. S.

Decomposition of Hydrocarbons of High Molecular Weight at a Moderate Temperature. By CARL ENGLER (*Ber.*, 1897, 30, 2908—2920).—The residues from the distillation of petroleum consist of unsaturated compounds, chiefly olefines and the products of their polymerisation. The oils which boil above 200° decompose when heated either in an open vessel or under pressure, the lower members of the paraffin series, together with olefines, naphthenes, and aromatic hydrocarbons, being formed, whilst the residue becomes still poorer in hydrogen. Several instances of this decomposition have been studied.

[With L. JEZIORANSKI.]—Two portions of the residue from Galician petroleum, remaining after the removal of all hydrocarbons boiling below 200°, were fractionally distilled, one at atmospheric pressure, the other under a pressure of 24—30 mm. The fractions thus obtained were again submitted to rectification. The distillates obtained under diminished pressure were practically unaltered by this second rectification. Those obtained at the ordinary pressure, on the other hand, began to boil at a much lower temperature than during the first distillation, more than 50 per cent. of each fraction passing over before the temperature was attained at which the fraction originally began to boil; thus a fraction which originally was collected between 315° and 330°, began to boil in the second rectification at 80°, and 30 per cent. of it passed over below 200°. The fractions obtained originally at the highest temperatures appear to yield the hydrocarbons of lowest boiling point. In another experiment, a heavy petroleum residue from Java petroleum, beginning to boil at 400°, was heated for some days in a flask connected with a reflux condenser, and the products of low boiling point were examined; these only amounted to a small percentage of the oil, and consisted of 41 per cent. of unsaturated and 59 per cent. of saturated hydrocarbons. Similar results were obtained by heating the oil in sealed tubes at 400°; the residue contained a carbonaceous deposit.

[With H. GRÜNING.]—The oils obtained by "cracking" petroleum, in order to obtain oils suitable for burning, have a sp. gr. = 0·8769 at 15°, and consist chiefly of olefines and paraffins, members of both series containing from 6 to 10 atoms of carbon having been isolated. In addition to these, benzene, toluene, xylene, mesitylene and ψ-cumene were isolated as nitro-compounds. It is also probable that naphthenes were present in small quantities.

[With C. SCHNEIDER.]—The oils obtained by distilling heavy petro-

leum under a pressure of about 6 atmospheres (Krey, German Patent 37728) have a sp. gr. = 0·8301, and closely resemble the foregoing in composition. A. H.

Decomposition of Chloroform, Bromoform and Chloral by Aqueous Solutions of Potassium Hydroxide. By ALEXANDRE DESGREZ (*Compt. rend.*, 1897, **125**, 780—782).—Chloroform is decomposed at the ordinary temperature by an aqueous solution of potassium hydroxide (1 : 8), the products being carbonic oxide, potassium chloride and water; the decomposition is accelerated by the action of light and also by heating gently. Solid potassium hydroxide does not decompose dry chloroform in a similar manner. Methylchloroform, phenylchloroform, methylenic chloride and carbon tetrachloride give no similar reaction with aqueous potash.

Bromoform decomposes in the same way as chloroform, but more slowly, by reason of its smaller solubility, and iodoform, being insoluble, is not decomposed at all. Chloral, on the other hand, is decomposed more rapidly than chloroform, the first stage in the reaction (production of potassium formate and chloroform) developing sufficient heat to accelerate the completion of the change.

Alkali carbonates and alkali hydrogen carbonates produce no analogous decomposition.

The liberation of carbonic oxide under the conditions specified is a much more characteristic reaction for chloroform than those commonly employed. C. H. B.

Electrolytic Preparation of Iodoform. By FRITZ FOERSTER and W. MEVES (*J. pr. Chem.*, 1897, [ii], **56**, 353—363. Compare Elles and Herz, *Zeit. elektrochem.*, **4**, 113).—The cell used was a battery-jar of 500 c.c. capacity, closed with an indiarubber bung. The electrodes were three parallel sheets of platinum foil; the middle one was the anode and had an area of 85 sq. cm.; the cathodes were enclosed in a wrapping of parchment paper. Between the electrodes were two tubes for leading in gas, and there was also a tube for leading away the gases evolved. A copper and a gas voltameter were also inserted in the circuit; the former for measuring the total amount of electricity that had passed during the experiment, whilst the latter made it possible to ascertain at any moment how the cell was working, the volume of gas evolved in it being compared with that evolved in the cell. The charge consisted of 400 c.c. of a solution containing 60 grams of potassium iodide, 20 grams of sodium carbonate and 80 c.c. of alcohol, the whole being kept at 60—65° by immersing the cell in a water bath at that temperature. The current density was as a rule 2 ampères per sq. dm., and to obtain a current of 2 ampères a potential difference of 2 volts was necessary. Every 8 ampère-hours the iodoform was removed, and the amount of potassium iodide to which it corresponded was added, together with 20 c.c. of alcohol.

The formation of iodoform takes place according to the equation, $C_2H_6O + H_2O + 10I = CHI_3 + 7HI + CO_2$; no formic acid could be detected. It will be seen that for every $7HI + CO_2$ formed at the anode 10KOH are formed at the cathode; the excess of 1KOH must be converted into carbonate by passing a slow current of carbonic anhydride

into the cell, so as to keep the colour of the solution pale yellow. In the presence of potassium hydroxide, considerable quantities of iodate are formed, and some acetic acid. When the proper precautions are observed, the yield of iodoform is equivalent to 80—90 per cent. of the electricity that has passed through the cell; it diminishes, however, when the potassium carbonate has accumulated largely in the solution. After a time, then, it is better to continue the electrolysis without further addition of potassium iodide; in this way, some 80 per cent. of the total iodide used can be converted into iodoform.

C. F. B.

Silver Cyanamide. By PAUL LEMOULT (*Compt. rend.*, 1897, **125**, 782—784).—Silver cyanamide is obtained by adding an aqueous solution of cyanamide to an ammoniacal solution of silver nitrate, treating the precipitate with nitric acid, reprecipitating with ammonia, and repeating this process until a pure product is obtained. It is insoluble in water even when heated, but is slightly soluble in hot dilute ammonia.

The action of ammoniacal silver nitrate on cyanamide solution develops + 9·64 Cal. The decomposition of silver cyanamide by nitric acid, absorbs − 11·2 Cal., and from these and other experiments in which silver cyanamide was decomposed by hydrochloric acid, it follows that $C + N_2 + Ag_2 = CN_2Ag_2$ solid, absorbs − 52·0 Cal. This value agrees with the explosive properties of silver cyanamide when heated in air. It is noteworthy, however, that, in absence of oxygen, it can be heated to 300° without undergoing any change. C. H. B.

Chlorocyanuramide. By PAUL LEMOULT (*Compt. rend.*, 1897, **125**, 822—824).—Chlorocyanuramide, $C_3N_3(NH_2)_2Cl$, obtained by the action of ammonia on cyanuric chloride, crystallises in very slender needles, very slightly soluble in water. Its heat of combustion as determined in the calorimetric bomb is 2758·2 cal., and hence the molecular heat of combustion is + 401·3 Cal. at constant volume and + 400·3 Cal. at constant pressure. Its heat of formation at constant pressure is, therefore, + 25·6 Cal. and it follows that $C_3N_3Cl_3$ sol. $+ 4NH_3$diss. $= 2NH_4Cl$ diss. $+ C_3N_5H_4Cl$ sol. develops + 81·7 Cal. The formation of the chlorocyanuramide, which is intermediate between cyanuric chloride and cyanuramide, is to be attributed to its insolubility. When cyanuric chloride and aqueous ammonia are heated in a sealed tube at 150°, the former is completely coverted into cyanuramide. It is noteworthy that the difference between the heats of formation of cyanuric chloride and chlorocyanuramide, 107·9 Cal., representing the thermal effect of the substitution of $2NH_2$ for 2Cl, is practically identical with the corresponding value in the case of acetic acid. C. H. B.

Preparation of Acetals. By EMIL FISCHER and GEORG GIEBE (*Ber.*, 1897, **30**, 3053—3059).—Both aliphatic and aromatic aldehydes can be converted into the corresponding acetals by the aid of dilute solutions of hydrogen chloride in the requisite alcohol. Diethylacetal diethylpropionacetal, and dimethylmethylal are readily obtained by the aid of 1 per cent. solutions of hydrogen chloride in alcohol.

To prepare *glycoldimethylacetal*, $OH\cdot CH_2\cdot CH(OMe)_2$, a larger quantity of alcohol must be taken, and the mixture heated for a longer time; it

boils at 158—159° (corr.) and resembles glycoldiethylacetal in all its properties. Glucoside-like products were not obtained.

Acraldehyde with a 0·5 per cent. solution of hydrogen chloride in ethylic alcohol yields triethoxypropane. Acraldehyde dibromide does not readily react at the ordinary temperature with a 1 per cent. solution of hydrogen chloride in ethylic alcohol, but on heating at 100° for 40 hours, the substance, $OEt\cdot C_2H_3Br\cdot CH(OEt)_2$, is obtained; it boils at 103—104° (corr.) under a pressure of 14 mm. and has a sp. gr. = 1·185 at 15°. Benzodiethylacetal is obtained when benzaldehyde is heated with the 1 per cent. solution for 60 hours at 100°; the yield is about 50 per cent. Nitrobenzaldehydes react more readily than benzaldehyde itself.

Paranitrobenzodimethylacetal, $NO_2\cdot C_6H_4\cdot CH(OMe)_2$, distils at 294—296° (corr.) under a pressure of 774 mm. On cooling, it solidifies and then melts at 23—25°. The corresponding *orthonitro*-compound boils at 274—276° at a pressure of 762 mm., but is partially decomposed at the same time. Anisaldehyde reacts in pretty much the same manner as benzaldehyde; the *acetal* boils at 253° (corr.) under a pressure of 764 mm. Its sp. gr. = 1·078 at 14°.

Piperonaldimethylacetal boils at 271—272° (corr.) under 757 mm. pressure; the yield is only 35 per cent. of the theoretical.

Salicylaldehyde, parahydroxybenzaldehyde, and vanillin give little or no acetal when heated for several days with alcoholic hydrogen chloride. J. J. S.

Decomposition of Galactose. By ALFED WOHL and ERNST LIST (*Ber.*, 1897, 30, 3101—3108).—It has been shown previously (Abstr., 1893, i, 292) that, when the oxime of *d*-glucose is converted into a nitrile and hydrogen cyanide subsequently abstracted, *d*-arabinose is formed. Further researches have now shown that when the oxime of *d*-galactose (Abstr., 1888, 40) is treated in a similar manner, the product is Fischer and Bromberg's lyxose (Abstr., 1896, i, 348). Galactosoxime was obtained by a method similar to that adopted for the preparation of glucosoxime (*loc. cit.*); when boiled with anhydrous sodium acetate and acetic anhydride, it yields *pentacetylgalactonic nitrile.* The dark-coloured substance which is thrown down when the product of the above reaction is poured into the requisite amount of sodium carbonate solution is washed well with water, extracted several times with ether, and the residue from the ethereal extract crystallised repeatedly from dilute alcohol. It forms colourless crystals, melts at 135° (uncorr.), and is only sparingly soluble in water, moderately in cold alcohol, readily in hot alcohol, benzene, ether, or chloroform. When treated with silver oxide and excess of ammonia, it yields the acetamide derivative which melts and decomposes at 222—226° (uncorr.); in most of its properties this compound resembles the acetamide derivative of *d*-arabinose. The corresponding pentose could not be obtained by exactly the same method as was used for the preparation of *d*-arabinose. The method adopted was as follows: the acetamide derivative (10 grams) was heated with 200 grams of N sulphuric acid and 600 grams of water for 2 hours in a reflux apparatus, and then heated with an excess of barium carbonate; the clear filtrate was evaporated

under reduced pressure to 20 c.c., diluted with 30 c.c. of 6 N sulphuric acid, extracted 15—20 times with ether in order to remove acetic acid, and the sulphuric acid precipitated with barium hydroxide, any excess of which was removed by the aid of carbonic anhydride. After filtration, the solution was evaporated under reduced pressure, when the sugar was obtained in the form of an uncrystallisable syrup. It gave the usual coloration with alkalis, reduced Fehling's solution, was lævorotatory, yielded fufuraldehyde on boiling with hydrochloric acid, and with phenylhydrazine gave xylosazone. Its identity with Fischer and Bromberg's lyxose was established by oxidising it to the lactone of lyxonic acid by Allen and Tollens' method (*Annalen*, 1891, **260**, 306).

J. J. S.

Action of the Halogens on Aliphatic Amines and Preparation of their Perhaloids. By JAMES F. NORRIS (*Amer. Chem. J.*, 1898, **20**, 51—64. Compare Abstr., 1896, i, 336).—The action of bromine and iodine on a number of aliphatic amines has been studied in order to determine whether the formation of iodine additive products and perbromides, such as those already described, is general. The action of iodine is being further investigated; so far, trimethylamine is the only amine which gives a di-iodo-additive product. Dimethylamine gives a compound containing two iodine atoms, but it has a constitution analogous to the bromides given below. Diamylamine gives the periodide $NH(C_5H_{11})_2,HI,I_2$.

A number of perbromides have been obtained, all having the general structure NR_3,HBr,Br, where one R may be hydrogen, and all give off 1 atom of bromine when dissolved in water. Primary amines apparently do not form perbromides.

By the action of chlorine on trimethylamine, a very unstable compound, having the appearance and odour of camphor, was obtained, but it could not be purified or analysed.

Attempts to prepare the compound NMe_3,ICl, described by Pictet and Krafft (Abstr., 1892, 1356), proved unsuccessful, as in all cases the product had the composition NMe_3I_2.

[With E. H. LAWS.]—*Dimethylammonium dibromide*, prepared by the action of bromine on dimethylamine hydrobromide, separates from alcoholic solution in yellow needles which melt at 93°, and do not decompose when heated to 200°. Bromine is without further action; chlorine, however, displaces one bromine atom, forming a *chlorobromide*, $NHMe_2,HCl,Br$, which can also be prepared by the action of bromine on dimethylamine hydrochloride.

Dimethylammonium tri-iodide, obtained by the action of iodine on dimethylamine hydriodide, crystallises from ethylic acetate in long needles, with a dark blue, steely lustre, melts at 97°, is decomposed by water into the hydriodide and free iodine, whilst treatment with potassium hydroxide yields iododimethylamine $(CH_3)_2NI$. The *di-iodide* was obtained as a dark-coloured oil.

Dimethylammonium chloriodide, $NHMe_2,HCl,I$, prepared by the action of iodine on methylamine hydrochloride dissolved in alcohol and chloroform, crystallises in dark red needles melting at 100°. Water liberates all the iodine, and potassium hydroxide forms iododimethyl-

amine. When treated with chlorine, a *substance*, $NHMe_2,HCl,I,Cl_2$, is obtained crystallising from alcohol in yellow needles. The *bromiodide* is a dark red, crystalline salt melting at 98—99°.

[With F. M. SMALLEY.]—*Trimethylammonium chloriodides.* The salt containing two halogen atoms is obtained when iodine monochloride acts on trimethylamine, as dark, reddish-brown needles melting at 84°. Water liberates iodine. A second *salt*, of the composition NMe_3,HCl,ICl_2, is produced when iodine trichloride is used instead of the monochloride; this melts at 168°, and is decomposed by water, with liberation of chlorine and iodine. The *chlorobromide* crystallises in yellow needles, and dissolves in water with liberation of bromine; the *bromiodide*, which crystallises in maroon needles, melts at 89°, and gives up iodine when acted on by water.

[With A. E. KIMBERLY.]—*Diethylammonium dibromide* crystallises in reddish-yellow needles, and when treated with potassium hydroxide yields a heavy, yellow, insoluble oil, which is still under investigation. The corresponding *dipropyl* and *tripropyl* compounds are crystalline substances, and the *diamyl* compound is a red oil.

When bromine acts on trimethylamine or its hydrobromide, a red oil is obtained which cannot be purified without decomposition. Tricetylamine is not acted on by bromine. A. W. C.

Crystalline Forms of the Platinochlorides of Diamines. By JOSEPH A. LE BEL (*Compt. rend.*, 1896, **125**, 351—354).—The author has examined salts of the type $(NH_2RR')_2PtCl_6$, and also double salts such as $(NH_2Me_2,NH_2Pr_2)PtCl_6$. The following method was adopted in order to determine whether any two given diamines formed such a double salt. 0·1 gram of one platinochloride was mixed with an equivalent quantity of the platinochloride of the second, about three-fourths was allowed to crystallise, and the sp. gr. of the crystals determined by the aid of ethylenic dibromide which was diluted with light petroleum until the crystals floated in equilibrium. If no double salt was formed, the original compounds were present, and the densities were little altered. If the substance was a double salt, its sp. gr. lay between those of the two original salts. The densities, axial relations, $a:b:c$, and inclination β of a large number of the platinochlorides of diamines are given. J. J. S.

Constitution of Hexamethylenetetramine. By GEORG COHN (*J. pr. Chem.*, 1897, [ii], **56**, 345—352).—The author proposes the formula $\underset{CH_2:C-}{\overset{NH}{|}}\!\!>CH\cdot CH(NH_2)\cdot CH(NH_2)\cdot CH:NH$ as affording the best expression of the reactions of hexamethylenetetramine (which is obtained by the action of ammonia on formaldehyde), and shows how these reactions can be explained by its means. Incidentally, the formula $NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH:NH$ is assumed for trimethylenetriamine. The points of which a formula for hexamethylenetetramine must afford an explanation are (1), the relation of the substance to the sugar group; (2), the different function of the nitrogen atoms; (3), the numerous additive products and their different stability; (4), the formation of tri- and pent-amine derivatives. C. F. B.

Isonitramines, and their Resolution into Hyponitrous Acid. By ARTHUR R. HANTZSCH and A. SAUER (*Annalen*, 1897, **299**, 67—99. Compare Abstr., 1897, ii, 25).—Hydroxyurethane *benzyl ether*, $COOEt\cdot NH\cdot OCH_2Ph$, obtained by agitating ethylic chlorocarbonate with α-benzylhydroxylamine, crystallises from alcohol in white plates, and melts at 31°. The substance dissolves readily in ether, more sparingly, however, in alcohol, and with still greater difficulty in water. The *nitroso*-derivative boils at 106° under a pressure of 35 mm., and resists the action of cold acids; it decomposes when distilled in an atmosphere of steam. Aqueous and alcoholic alkalis resolve the nitroso-derivative into benzaldehyde and ethylic alcohol, nitrogen and carbonic anhydride being eliminated.

Benzenesulphonhydroxamic acid *benzyl ether*, $SO_2Ph\cdot NH\cdot OCH_2Ph$, is prepared from benzenesulphonhydroxamic acid (Piloty, Abstr., 1896, i, 555) and α-benzylhydroxylamine; it crystallises from alcohol in white needles, and melts at 107°. The impure nitroso-derivative, which could not be isolated, yields benzaldehyde and nitrogen when treated with sodium carbonate.

Attempts to prepare the nitroso-derivative of hydroxyurethane (Hantzsch, Abstr., 1894, i, 364) were also unsuccessful, treatment of hydroxyurethane with nitrous acid giving rise to a yellow oil which decomposes in the desiccator; aqueous ammonia dissolves the oil, with liberation of nitrogen, acetaldehyde being produced. Benzhydroxamic acid and acethydroxamic acids, however, yield no isonitramine, nitrous acid converting them into hydroxylamine and benzoic and acetic acids respectively; hyponitrous acid was not recognised among the products, nor was this substance produced by the action of nitrous acid on benzenesulphonehydroxamic acid.

Dimethylamidocarboxylic chloride, $NMe_2\cdot COCl$, is prepared by passing dry carbonyl chloride over dry dimethylamine hydrochloride, which is carefully heated in a small distilling flask, the receiver being cooled with ice; it is a colourless liquid which boils at 165°, and is indifferent towards alkalis at 0°, being resolved into carbonic anhydride and dimethylamine hydrochloride when heated. On agitating the substance with free, aqueous hydroxylamine, the liquid acquires the properties of a hydroxamic acid. It develops an intense violet coloration with ferric chloride, reduces silver nitrate, and yields a slimy, green copper salt; the dimethylhydroxycarbamide has not been isolated. The *benzyl ether*, $NMe_2\cdot CO\cdot NH\cdot OCH_2Ph$, is an oil which does not solidify at −15°; the *hydrochloride* is precipitated on passing hydrogen chloride into its ethereal solution.

Dimethylnitrosohydroxycarbamide (*dimethylcarbonylisonitramine*), $NMe_2\cdot CO\cdot N\cdot N_2O_2H$, is prepared by passing nitrous anhydride into the liquid obtained by agitating dimethylamidocarboxylic chloride with hydroxylamine until it no longer develops colour with ferric chloride; it is a yellow oil, which mixes in every proportion with water, being extracted from the solution by ether. It decomposes when gently heated. Although indifferent towards acids, the substance is very sensitive towards alkalis, caustic potash converting it into potassium hyponitrite and dimethylamine, with elimination of carbonic anhydride, and it is decomposed also by ammonia.

Diethylamidocarboxylic chloride, $NEt_2{\cdot}COCl$, boils at 186°, and in behaviour resembles the methyl-derivative.

When carbonyl chloride is passed into an ice cold solution of hydroxylamine, the liquid acquires the properties of a hydroxamic acid, but the product is very unstable. It is immaterial whether one molecular proportion of hydroxylamine is employed, or twice this amount, the liquid in each case developing an intense violet coloration with ferric chloride, and yielding with copper acetate a highly unstable copper salt which liberates gas, and passes into cuprous oxide. These facts point to the formation of *hydroxycarbaminic*, $OH{\cdot}CO{\cdot}NH{\cdot}OH$, or *carbohydroxamic acid*, $(OH)_2{\cdot}C{:}NOH$, instead of dihydroxycarbamide, $CO(NH{\cdot}OH)_2$.

On treating with nitrous acid the liquid obtained by the action of carbonyl chloride on aqueous hydroxylamine, carbonic anhydride, nitrous oxide, and water are produced. If, however, the operation is carried out in methylic alcohol, evidence of the production of hyponitrous acid is forthcoming.

The authors have estimated the amount of ammonia arising from the decomposition of hyponitrous acid, and find that the quantity is variable and very small; it probably arises from ammonium salts contaminating the silver hyponitrite from which the free acid is prepared. Contrary to the statement of Thum (Abstr., 1894, ii, 13), it is not possible to estimate hyponitrous acid by titration with potassium permanganate.

Hyponitrous acid is obtained by the action of nitrous acid on hydroxylamine or hydroxycarbamide dissolved in methylic alcohol.

M. O. F.

Salts of Nitroparaffins, and Acylated Derivatives of Hydroxylamine. By LAUDER W. JONES (*Amer. Chem. J.*, 1898, **20**, 1—51. Compare Abstr., 1896, i, 460).—When sodium isonitroethane, prepared by the action of sodium ethoxide on an alcoholic solution of nitroethane, is acted on by benzoic chloride in aqueous or ethereal solution, a very complicated mixture of substances is produced. In the first place, a derivative, $CHMe{:}NO{\cdot}OBz$, of isonitroethane is formed by replacement of sodium by the benzoyl group; this cannot be isolated, but is immediately converted by intramolecular oxidation into the *benzoate of acethydroxamic acid*, $CH_3{\cdot}CO{\cdot}NH{\cdot}OBz$, existing in two forms, which can be separated by the difference in their solubility in ether; the one forms well developed crystals melting at 98—99°, the other flat, transparent crystals melting at 69—70°. After a time, the form of lower melting point, which is possibly a hydroximic acid, becomes opaque, and passes completely into the form of high melting point. It is decomposed by boiling water or dilute alkalis into benzoic acid and acethydroxamic acid, and on heating yields benzoic acid, methylcarbimide, and a brown residue. A specimen of the benzoate prepared by the action of benzoic chloride on pure acethydroxamic acid was also found to exist in two modifications corresponding exactly in melting points and crystalline forms with the above.

In the original reaction, this benzoate immediately acts on the isonitroparaffin salt, regenerating nitroethane and forming the sodium

salt of the benzoate of acethydroxamic acid, and the latter, in presence of benzoic chloride, reacts in two ways, giving rise:—(1) to the *benzoate of benzoylacethydroxamic acid*, OBz·CMe⁚N·OBz, a thick oil that could not be made to crystallise; this is decomposed by alcoholic potash into benzoic acid and the benzoate of acethydroxamic acid, thus proving its constitution, and:—(2) to *α-benzoyl-β-acetylbenzoylhydroxylamine*, NAcBz·OBz, a neutral substance occurring in transparent, monoclinic crystals melting at 68—69°; this is insoluble in alkalis and water, but soluble in alcohol, ether, and light petroleum. On treatment with alcoholic potash, it is converted into the benzoate of benzhydroxamic acid and acetic acid, which fact, in conjunction with the synthesis of this hydroxylamine derivative from the benzoate of benzhydroxamic acid and acetic chloride, conclusively proves its constitution. *Acetobenzhydroximic benzoate*, OBz·N⁚CPh·OAc, forms needle-shaped crystals melting at 84—85°, soluble in alcohol and ether, but insoluble in water.

It was expected that the results obtained by the action of ethylic chlorocarbonate on isonitroethane would be similar to those of the action of benzoic chloride; but although derivatives of acethydroxamic acid are produced, the reaction is complicated by the evolution of carbonic anydride, and has not been thoroughly investigated. In order, however, to become acquainted with the possible derivatives, the following compounds were prepared synthetically.

Ethylic acethydroxamic carbonate, COMe·NH·O·COOEt, prepared by the action of ethylic chlorocarbonate on acethydroxamic acid, crystallises from ether in long, flat needles melting at 71—72°. When left in contact with ferric chloride, it shows an intense colour reaction, is decomposed by alkalis and alkali carbonates, and on distillation gives carbonic anhydride, an intense odour of a carbimide, and a pale yellow oil boiling between 180 and 220°.

Ethylic ethylnitrolic carbonate, NO_2·CMe⁚N·O·COOEt, is a yellow oil boiling at 143—144° (17 mm.), or with considerable decomposition at 210—215° under the ordinary pressure. Boiling water decomposes it, liberating carbonic anhydride and forming ethylnitrolic acid and its decomposition products.

The action of benzoic chloride on sodium isonitromethane presents difficulties which have not yet been overcome, but there is no doubt that the benzoate of benzoylformhydroxamic acid is produced with formation of a similar salt of formhydroxamic acid as intermediate product.

Formhydroxamic acid, COH·NH·OH, prepared by the action of ethylic formate on a mixture of hydroxylamine hydrochloride and sodium methoxide, crystallises in large, thin, transparent plates with a brilliant pearly lustre and striated surfaces, and melts at 81—82°. It is soluble in warm acetone, from which it can be obtained in groups of thick crystals, but on standing these redissolve, undergoing decomposition, the exact nature of which has not been fully determined. The pure acid is not hygroscopic, and is stable, but when heated slightly above its melting point it explodes, giving off a vapour smelling strongly of hydroxylamine; this fact, taken in conjunction with its stability, supports the above oxam-formula rather than the oxime form, OH·CH⁚N·OH. The *sodium* salt prepared by the action of sodium ethoxide on an alco-

holic solution of the acid, separates as a fine, white, very hygroscopic powder, which explodes on heating; the *copper*, *lead*, and *mercury* salts are also explosive. The *benzoate*, prepared by the action of benzoic chloride on the acid, crystallises from ether in well developed prismatic needles melting at 76·5—77·5°; it is decomposed by caustic soda into benzoic and formhydroxamic acids, and by heat into benzoic acid and carbimide. During the preparation of this benzoate, *benzoylformhydroxamic benzoate*, OBz·CH⁚N·OBz, is also obtained; this crystallises from a mixture of ether and light petroleum in delicate, colourless needles melting at 109—111°. It is insoluble in alkalis, but is decomposed by them, more especially on heating.

Experiments on the action of mercuric chloride on sodium isonitromethane, and of the action of alkylic iodides on the mercury salts thus formed, are described; it is shown that these salts cannot be derivatives of carbonic anhydride oxime of the formula CO⁚N·OH, as was considered probable by Nef.

In discussing the formulæ of the salts of the nitroparaffins, the author points out that it is impossible to explain their reactions and properties, more especially the intramolecular oxidation which they undergo, if the ring grouping proposed by Hantzsch (Abstr., 1896, i, 353, 672) is adhered to. He therefore assigns to them Nef's open formulæ (*ibid.*, 461).

Hydroxyurethane (*carbethoxyhydroxamic*) *methylic ether*,

EtO·CO·NH·OMe,

is formed when methylic iodide acts on the potassium derivative of hydroxyurethane prepared by a slight modification of the method employed by Hantzsch (Abstr., 1894, i, 364); it is a colourless liquid boiling at 186—188°, and gives no reaction with ferric chloride. When treated with concentrated hydrochloric acid, it is decomposed into carbonic anhydride, ethylic chloride, and α-methylhydroxylamine hydrochloride. The corresponding *ethylic* ether boils at 195—196° (95—97° at 17 mm.); hydrochloric acid decomposes it into carbonic anhydride, ethylic chloride, and α-ethylhydroxylamine hydrochloride. It was hoped that ethers of the oxime of carbonic anhydride would be obtained by the action of phosphorus pentachloride on this substance, but owing to the instability of the product, it has been impossible to decide this point. The *benzylic* ether, a thick, colourless oil boiling at 171—172° (11 mm.), is soluble in alkalis, and is reprecipitated undecomposed by acids; concentrated hydrochloric acid decomposes it with production of α-benzylhydroxylamine hydrochloride. The *benzoate* forms soft, fibrous crystals melting at 38—39° and boiling at 180—190° (20 mm.); when treated with benzoic chloride, it is converted into the dibenzoyl derivative of hydroxyurethane, which separates from a mixture of ether and light petroleum in transparent, prismatic crystals melting at 72—73°.

αβ-Dimethylcarbethoxyhydroxylamine [*hydroxymethylurethane methylic ether*], COOEt·NMe·OMe, is also produced by the action of methylic iodide on carbethoxyhydroxamic acid as a colourless oil boiling at 150—155°; when treated with concentrated hydrochloric acid, carbonic anhydride, ethylic chloride, and *α-dimethylhydroxylamine hydrochloride*, NHMe·OMe,HCl, are produced. The latter crystallises from

chloroform in long, coarse, prismatic needles melting at 115—116°; it is not hygroscopic, is volatile at 100°, and does not reduce ammoniacal silver nitrate or Fehling's solution. The *platinochloride* separates from alcohol in red, prismatic crystals melting and decomposing at 180°. The *free base* is a colourless, very volatile liquid, boiling at 42·2—42·6°, of a sweet, rather unpleasant odour, and does not reduce silver nitrate or Fehling's solution.

αβ-Diethylcarbethoxyhydroxylamine [*hydroxyethylurethane ethylic ether*] *hydrochloride* is with difficulty obtained in long, fibrous needles melting at 123—124°. The *free base* is an oil boiling between 160° and 180°. A. W. C.

The Direct Elimination of Carbonic Oxide, and the Reaction of this with Water. By CARL ENGLER and J. GRIMM (*Ber.*, 1897, **30**, 2921—2926. Compare Abstr., 1893, i, 512).—Many organic compounds decompose when heated, carbonic oxide being formed directly, without any reduction of carbonic anhydride (compare Phillips, *Trans. Amer. Phil. Soc.*, **17**, 1). Formic acid, for instance, at 150—160° yields a gas which consists of 98·8 of carbonic oxide and 1·2 per cent. of carbonic anhydride. Ethylic formate decomposes at 300°, yielding a mixture of carbonic oxide, 18·2; carbonic anhydride, 29·5; ethylene, 7·2, and hydrogen, 45·1 per cent.: amylic formate decomposes in a similar manner at 300°, but yields amylene instead of ethylene, whilst ethylic oxalate at 200° yields carbonic oxide, 48·4; carbonic anhydride, 43·8, and olefines, 7·8 per cent.

Benzoin at 280° yields a gas containing 92 per cent. of carbonic anhydride and 8 of carbonic oxide; the oily residue produced in this case contains diphenylmethane, deoxybenzoin, benzil, and a trace of benzaldehyde. Benzoylacetone does not yield any gas at 300°.

Pure carbonic oxide, carefully freed from oxygen, does not react with water vapour at 250°, but does react at 300°, producing carbonic anhydride. It is probable that the formation of carbonic anhydride in the foregoing decompositions of various substances is due to this secondary reaction between the carbonic oxide, which is first produced, and water vapour. A. H.

Volatile Acids of the Acetic Series from the Suint of Wool. By A. BUISINE and P. BUISINE (*Compt. rend.*, 1897, **125**, 777—780). —When the water used for the desuintage of wools is allowed to remain exposed to the air for a few days, it undergoes, as the authors have previously shown, a special fermentation which results in the formation of volatile acids of the acetic series. After fermentation, one sample of sp. gr. = 1·079 was found to have the following composition per litre: total residue, 153·4; ammonia (as carbonate), 1·5; total nitrogen, 4·5; potassium carbonate (as such), 7·6; volatile acids (calculated as H_2SO_4), 16·0; fatty matter, 15·5; inorganic matter, 77·4; total potassium carbonate obtainable, 65·5 grams.

In order to extract the fatty acids, the liquid is boiled to expel ammonia, which is collected, and is then acidified with sulphuric acid, and treated with a current of steam, the acids of higher molecular weight distilling first. The percentage composition of the acid mixture obtained from the suint referred to above was acetic acid, 60; pro-

pionic acid, 25 ; butyric acid, 5 ; valeric acid, 4 ; caproic [hexoic] acid, 3 ; benzoic acid, 3, and traces of formic and caprylic [octoic] acids and phenol, the total yield per litre being 20·6 grams. The crude mixture of acids is very suitable for the production of "acetone oil."

The acetic acid can be separated by adding to an aqueous solution of the mixed acids a limited quantity of calcium carbonate, which combines exclusively with the acetic acid, and the other acids can be distilled off in a current of steam.

The sulphuric acid is removed as potassium sulphate by concentrating the liquid from which the acids have been removed, or the residue from this liquid may be mixed with calcium carbonate before being heated. In the latter case, on treatment with water, all the potassium dissolves as carbonate and the sulphuric acid remains undissolved as calcium sulphate. C. H. B.

Conversion of Butyric into Isobutyric Acid. By EMIL ERLENMEYER, sen. (*Ber.*, 1897, **30**, 2956—2962. Compare Hutzler and V. Meyer, this vol., i, 62).—The author admits that he is not certain that the calcium butyrate used by him was free from isobutyrate; he thinks it probable, however, that the calcium salt obtained by Hutzler and V. Meyer, which in appearance and properties resembled calcium butyrate, was a double isobutyrate and butyrate. To show that the conversion of butyrate into isobutyrate may take place, the author refers to the conversion of benzil into benzilic acid. of pinacone into pinacoline, reactions in which OH changes place with H. It is considered that a similar interchange between CH_3 and H may also be possible, for example, the formation of isopropylic alcohol from normal propylamine (*Annalen*, 1876, **181**, 128, and this Journal, 1876, ii, 182), and the conversion of normal propylic bromide into isopropylic bromide by the aid of aluminium bromide (*Ber.*, 1879, **12**, 2279) are cited as cases. J. J. S.

A seemingly General Reaction of α-Amido-acids of the Formula NH_2·CHR·COOH. By EMIL ERLENMEYER, jun. (*Ber.*, 1897, **30**, 2896—2899. Compare Abstr., 1896, i, 305; 1897, i, 480)—The behaviour of glycocine towards benzaldehyde (*loc. cit.*) is exhibited also by other α-amido acids, such as aspartic acid, leucine, and tyrosine. M. O. F.

Stereoisomeric Chlorobromosuccinic Acids. By PAUL WALDEN (*Ber.*, 1897, 30, 2883—2888).—*Fumaroid chlorobromosuccinic acid*, COOH·CHCl·CHBr·COOH, is prepared by heating chlorofumaric acid with a solution of hydrogen bromide in glacial acetic acid at 125° until completely dissolved, and subsequently at 135—140° during 2 hours; it melts and decomposes at 235—237° in a sealed capillary tube. When mixed with phosphoric anhydride and distilled, the acid yields chloromaleic acid, which is also produced, along with chlorofumaric acid, when chlorobromosuccinic acid is boiled with water (5 parts); methylic alcoholic potash converts it into mesotartaric acid. The *ethylic* salt is prepared by warming the acid with ethylic alcohol and a small quantity of concentrated sulphuric acid, and it is also produced when ethylic chlorofumarate is heated on the water bath with a fuming solution of

hydrogen bromide in glacial acetic acid; it crystallises from petroleum in feathery aggregates of small needles, and melts at 59—60°.

Maleinoid chlorobromosuccinic acid is prepared by saturating with chlorine a solution of bromine in chloroform, adding maleic anhydride, again passing chlorine into the liquid, which is then exposed to bright sunlight; the anhydride which is obtained on evaporating the chloroform yields the acid when dissolved in cold water. The acid crystallises from water or ethylic acetate in plates, and dissolves readily in common solvents; it melts and decomposes at 165° when heated in a sealed capillary tube. Distillation with phosphoric anhydride converts it into chloromaleic acid, and protracted treatment with boiling water gives rise to chlorofumaric acid; when gently heated with fuming hydrochloric acid, it is converted into fumaroid chlorobromosuccinic acid. The *anhydride* crystallises from chloroform, and melts at 78°; the *ethylic* salt is an oily liquid.

Directions for the preparation of chloromaleic and bromomaleic acids are given in the paper, which concludes with a synopsis of the behaviour of dibromosuccinic, dichlorosuccinic, chlorobromosuccinic (fumaroid and maleinoid), isodibromosuccinic, and isodichlorosuccinic acids and their derivatives. M. O. F.

α-Amidoethylidenesuccinimide and Acetylsuccinimide. By Icilio Guareschi (*Chem. Centr.*, 1897, i, 283; from *Atti Real. Accad. Torrino*, 31).—Ethylic α-amidoethylidenesuccinate,

$$NH_2\cdot CMe\colon C(COOEt)\cdot CH_2\cdot COOEt,$$

was obtained by Conrad and Epstein (Abstr., 1888, 253) from ethylic acetylsuccinate by the action of gaseous ammonia, and by Emery (Abstr., 1891, 544) from the same substance by saturated alcoholic ammonia at 0°. The author finds, however, that when aqueous ammonia (sp. gr. = 0·914) is used, *α-amidoethylidenesuccinimide*, $NH_2\cdot CMe\colon \begin{matrix} C\text{——}CO \\ | \\ CH_2\cdot CO \end{matrix}\!\!>\!NH$, is formed; this crystallises from water in prisms, and when heated darkens at 235—240° and melts at 274—275°. It is readily soluble in boiling water, sparingly in cold water and in alcohol, and nearly insoluble in ether. The *silver* derivative of the imide was analysed. On treating this with hydrochloric acid, ammonium chloride and *acetylsuccinimide*, $\begin{matrix} CHAc\cdot CO \\ | \\ CH_2\text{—}CO \end{matrix}\!\!>\!NH$, were obtained; the latter melts at 84—87°, and yields a *silver* derivative. No well-characterised ethyl derivative of α-amidoethylidenesuccinimide could be obtained, but an *acetyl* derivative was prepared; this crystallises from hot water in long needles, melts at 233—234°, and gives rise to a *silver* derivative, which, however, was not obtained pure.

W. A. D.

Some Pyrotartaric Alkylimides. Condensation of Tartaric Alkylimides with Acid Chlorides. By M. Kling (*Ber.*, 1897, 30, 3039—3043).—The pyrotartaric alkylimides, $\begin{matrix} CHMe\cdot CO \\ | \\ CH_2\text{—}CO \end{matrix}\!\!>\!NR$, are made by distilling the amine hydrogen salt with a certain excess of the amine. *Pyrotartarmethylimide* comes over at 223°; pyrotartar-

ethylimide boils at 222—223°, the yellowish *pyrotartarbenzylimide* at 315°, and *pyrotartarphenylimide* melts at 107°.

By heating acid chlorides, R′·COCl, with tartarimides,

$$\begin{matrix}CH(OH)\cdot CO \\ | \\ CH(OH)\cdot CO\end{matrix}\!>\!NR,$$

at 100°, derivatives of the type $\begin{matrix}R'\cdot COO\cdot CH\cdot CO \\ | \\ R'\cdot COO\cdot CH\cdot CO\end{matrix}\!>\!NR$ are obtained. *Dibenzoyltartarethylimide* melts at 159—160°; *phthalyltartarmethylimide* begins to melt and decompose at 180°. *Dicinnamoyltartarmethylimide* crystallises with benzene (1 mol.), and then melts at 80—81°; after the benzene has been driven off, it forms a vitreous mass which melts at 70—72°. This is named the α-variety; when crystallised from alcohol, or after prolonged lying in the air, it is obtained in crystals which melt at 95°, and are termed the β-variety; this is reconverted into the α-form by simple heating above its melting point. In 10 per cent. ethylic acetate solution, the α- and β-forms have the rotatory power 307·8° and 311·6° respectively. Two similarly isomeric dibenzoyltartarmethylimides have been described by Ladenburg (Abstr., 1897, i, 139).
C. F. B.

Interconversion of Optical Antipodes. By Paul Walden (*Ber.*, 1897, **30**, 3146—3151. Compare this vol., i, 176).—The action of silver carbonate on optically active halogen derivatives of succinic acid in aqueous solution converts them into malic acids which rotate the plane of polarisation in the same directions as the respective halogen derivatives. Alcoholic potash of certain concentration (1 : 4) eliminates halogen hydride, giving rise to inactive products, and reduction with sodium amalgam, in alcoholic solution, likewise yields an inactive solution. If, however, halogen is replaced by hydroxyl through the agency of less concentrated alcoholic potash (1 : 9), the optical antipodes of the malic acids obtained by the action of silver salts are produced. Aqueous potash and baryta have the same effect as alcoholic potash.
M. O. F.

Action of Formaldehyde on Carbamide. By Carl Goldschmidt (*Chem. Zeit.*, 1897, **21**, 460. Compare Abstr., 1897, i, 22).—Carbamide, when allowed to remain with an excess of formaldehyde (40 per cent. solution) in alkaline solution, yields a white precipitate, $C_3N_2O_3H_8 = CO(NH\cdot CH_2\cdot OH)_2$, which is soluble in hot water, and is precipitated by alcohol as a gelatinous mass. After two recrystallisations from water, it appears to be transformed into the compound $C_6N_4O_5H_{14}$.

In a neutral solution, the chief products are the above-mentioned soluble compound, $C_3N_2O_3H_8$, and a substance, $C_5N_4H_{12}O_4$, which is insoluble in water.
J. J. S.

1-Methyl- and 1 : 7-Dimethyl-uric Acids. By Emil Fischer and Hans Clemm (*Ber.*, 1897, **30**, 3089—3097).—Methylalloxan,

$$CO\!<\!\begin{matrix}NMe\cdot CO \\ NH—CO\end{matrix}\!>\!C(OH)_2,$$

(compare Hill, this Journal, 1876, ii, 509; and Fischer, Abstr., 1883, 356), which is best obtained by the oxidation of theobromine with hydrochloric

acid and potassium chlorate, may be isolated, by the aid of hydrogen sulphide, as dimethylalloxantin, which, after recrystallisation from water, is carefully oxidised by nitric acid back to methylalloxan. When its solution is evaporated under diminished pressure, methylalloxan crystallises in large, colourless, compact crystals; it turns red at about 100° and melts and decomposes at 156°.

1-*Methyluramil*, $CO<\begin{matrix}NMe\cdot CO\\NH—CO\end{matrix}>CH\cdot NH_2$, is obtained when methylalloxan (4 parts) is treated with a concentrated solution of ammonium sulphite (12 parts) for 6 hours at 80°. If rapidly recrystallised from hot water, it forms colourless plates, which, when moist, readily turn red. In its properties it resembles dimethyluramil (Techow, Abstr., 1895, i, 83).

When 1-methyluramil (1 part) is heated with pure potassium cyanate (1 part) and water (3 parts) on the water bath for some 5—10 minutes, until the deep red colour first produced disappears, and the mixture is then allowed to cool, *potassium methyl-ψ-urate* separates. The free *acid* crystallises from hot water in small, colourless needles, turns red at 200°, and melts and decomposes at about 220°. The yield is almost quantitative.

1-*Methyluric acid* is obtained when the pseudo-acid is boiled for a few minutes with 9 times its weight of 20 per cent. hydrochloric acid, and then heated on the water bath for an hour. The precipitated acid is best purified by conversion into its *magnesium* salt, $C_{12}H_{10}N_8O_6Mg + 7H_2O$, which can be readily recrystallised from boiling water. The acid crystallises in minute needles, turns brown at about 400°, and is carbonised at higher temperatures without melting; its extremely slight solubility in hot water (1 in 2050) differentiates it from 3-methyluric acid. The acid dissolves in an excess of caustic alkali, in warm ammonia, and in hot dilute barium hydroxide solutions. It is readily oxidised by nitric acid or chlorine water, and gives the murexide reaction. The authors consider that von Loeben's acid (this vol., i, 128) is merely a mixture of their acid with 3-methyluric acid.

1:3-Dimethyluric acid is obtained when the 1-methyl acid (1 gram) is dissolved in 1 c.c. of N potassium hydroxide, and is shaken with 0·8 gram of methylic iodide at 50° for $\frac{3}{4}$—1 hour; on adding hydrochloric acid, the dimethyl acid is precipitated together with a small quantity of the original monomethyl acid. The dimethyl acid is readily separated by solution in boiling water, and is identical with γ-dimethyluric acid prepared by Fischer and Ach (Abstr., 1896, i, 12). A mixture of 1:7-dimethyluramil and 1-methyluramil is obtained by the action of methylamine sulphite on methylalloxan; when the crude mixture is treated with potassium cyanate, a mixture of mono- and di-methyl-ψ-uric acids is obtained, and this, when warmed on the water bath for 2 hours with 20 per cent. hydrochloric acid, yields a mixture of 1-methyluric acid, and 1:7-*dimethyluric acids*. The dimethyl acid is much more readily soluble in boiling water (1 in 114) than the monomethyl acid; it crystallises in pointed prisms, often arranged in stars, and melts and decomposes at 390°. The *potassium*

salt, $C_7H_7N_4O_3K + H_2O$, is characteristic; the ammonium, barium, and silver salts are also described. J. J. S.

Tetramethyluric Acid. By Emil Fischer (*Ber.*, 1897, **30**, 3009—3014. Compare Abstr., 1884, 1310).—This acid, $C_9H_{12}N_4O_3$, is now found to melt at 223° (corr. 228°). It is monoclinic; $a:b:c = 1\cdot7686:1:2\cdot0079$; $\beta = 61° 20'$. When heated with 5 times its weight of phosphorus oxychloride for at least 10 hours at 160° in a sealed tube, it yields chlorocaffeine, $C_8H_9N_4O_2Cl$, melting at 186—188°; this is best isolated by evaporating the product of the action, extracting the residue with water, heating this second residue with 5 times its weight of hydrochloric acid (sp. gr. = 1·19) for 3 hours at 130°, evaporating the whole to dryness, extracting the residue with dilute aqueous soda, and crystallising what is left from alcohol. By passing chlorine into a 1 per cent. aqueous solution of tetramethyluric acid at 25°, allocaffeine is obtained; this is now found to melt at 203° (corr. 206°). By passing dry chlorine into a 5 per cent. solution of the acid in dry chloroform free from alcohol, an *oxytetramethyluric acid*, $C_9H_{12}N_4O_4$, melting at 224° (corr. 229°), is obtained. When tetramethyluric acid (1 mol.) is shaken for 3 hours at 15° with normal potassium hydroxide solution (2 mols.), a basic substance is obtained which melts at 165—167° (corr. 166—168°); this has the composition $C_8H_{14}N_4O_2$, and hence stands to tetramethyluric acid in the same relation as caffeidine to caffeine; for this reason it is named *tetramethylureidine*. C. F. B.

Constitution of Hexahydrobenzene. By Nic. Kijner (*J. pr. Chem.*, 1897, [ii], **56**, 364—372).—The author adduces further arguments in support of the identity of hexahydrobenzene with methylpentamethylene, and complains that his early recognition of this identity has been ignored. Fresh samples of hexahydrobenzene have been prepared by heating benzene with hydriodic acid of sp. gr. = 1·96 for 24 hours at 280°, and purifying the product by treatment with nitric acid; one boiled at 72—73° under 752 mm. pressure, had a sp. gr. = 0·7489 at 20°/0° and index of refraction $n_D = 1\cdot4101$ at 20°; the other boiled at 71—73°, and had a sp. gr. = 0·7648 at 0°/0°, 0·7486 at 20°/0°. Prolonged action of fuming nitric acid at 0° appears to convert hexahydrobenzene partially into formic, acetic, and glutaric acids; the dilute acid at 100° converts it into the nitro-derivative, $\begin{matrix}CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\end{matrix}\!\!>\!CMe\cdot NO_2$ of Markownikoff and Konowaloff (Abstr., 1895, i, 454). When aniline is reduced with hydriodic acid at temperatures approaching 300°, the product distils between 65° and 81°, and probably contains some hexamethylene in addition to hexahydrobenzene (methylpentamethylene). C. F. B.

Migration of the Iodine Atom during the Nitration of Aromatic Iodo-Derivatives. By Frédéric Reverdin (*Ber.*, 1897, **30**, 2999—3003. Compare Abstr., 1896, i, 475; 1897, i, 27).—The method of nitration adopted was to mix the derivative with nitric acid

of sp. gr. = 1·51 (usually with its own weight), and pour the mixture on to ice after a time. The iodonitrotoluene melting at 103° obtained by Beilstein and Kuhlberg (*Annalen*, **158**, 347) by nitrating orthoiodotoluene, is now shown to have the constitution [Me : I : NO_2 = 1 : 2 : 5], for it is identical with the product obtained by the diazo-reaction from 1 : 2 : 5-nitrotoluidine. From 1 : 2 : 4-nitrotoluidine, 1 : 2 : 4-*iodonitrotoluene* was obtained ; this is yellowish and melts at 51°. Pariodotoluene, when nitrated, yields iodonitrotoluene [Me : I : NO_2 = 1 : 4 : 2] as the main product, together with paranitrotoluene, a lemon-yellow substance (? di-iodonitrotoluene) melting at 112°, and an oil ; no migration of the iodine atom from the para- to the ortho-position takes place, such as is observed when pariodanisoil and phenetoil are nitrated.

The action of nitric acid on orth- and par-iodaniline and on pariodophenol results in the elimination of the iodine. From pariodacetanilide, the nitro-derivative of Michael and Norton (Abstr., 1878, 406) could not be obtained.

Methylic orthiodobenzoate, when nitrated, yields pale yellow *methylic iodonitrobenzoate* melting at 123°. From methylic pariodobenzoate another methylic iodonitrobenzoate was obtained ; this is yellow, but melts at 103·5°, and is therefore isomeric, and not identical, with the compound already described ; no migration of the iodine atom to the ortho-position can have taken place. C. F. B.

Double Salts of the Anilides with Cuprous Chloride and Cuprous Bromide. By WILLIAM J. COMSTOCK (*Amer. Chem. J.*, 1898, **20**, 77—79)—In studying the behaviour of certain of "Schiff's bases" towards cuprous chloride and bromide, the author wished to prepare derivatives of cuprous haloids which should be easily soluble in organic solvents and give up the haloids readily, and finds that the double salts with acetanilide fulfil these conditions.

The *double* salt of cuprous chloride and acetanilide has the composition $(NHPh\cdot COMe)_2,HCl,CuCl$, and is best prepared by adding its constituents to a hot mixture of glacial acetic and hydrochloric acids ; it crystallises from alcohol in beautiful, long prisms. Protracted boiling of the solution, however, causes the acetyl group to separate. When heated, it darkens at 140° and melts near 170° with violent decomposition. Freshly prepared, it is colourless, but when dry, acquires a yellowish tint. It does not lose hydrogen chloride in a vacuum over caustic potash, and can be heated at 100° without loss in weight. The *double* salt with cuprous bromide crystallises from alcohol in long, colourless, doubly terminated prisms, darkening when heated to 170°, and melting with decomposition at 185—195°.

With cuprous bromide, parabromacetanilide gives a *double* salt of composition similar to the above, separating from alcohol containing hydrogen bromide, in long, colourless prisms, which suffer no loss in weight when dried in a vacuum over sulphuric acid or caustic potash.

When formanilide is added to a solution of cuprous bromide in a mixture of formic and hydrobromic acids, a salt separates at once in well-developed, doubly terminated prisms, changing, however, after a few moments into small plates consisting of the double salt of aniline

and cuprous bromide. The corresponding *salt* of formoparatoluidide crystallises in colourless, flat prisms. A. W. C.

Action of Ethereal Salts on Aromatic Amines. By STEFAN VON NIEMENTOWSKI (*Ber.*, 1897, **30**, 3071—3073. Compare Hjelt, *Jahresberichte*, 1887, 1535).—Aniline reacts with ethylic acetate, yielding acetanilide and ethylic alcohol, but the reaction between ethylic acetate and aniline hydrochloride is quite different. When the salt (13 grams) is heated with ethylic acetate (9 grams) for 3 hours at 225°, the chief products are mono- and di-ethylaniline hydrochlorides and acetic acid.

The reaction appears to be a general one, aniline hydrochloride and ethylic formate yield ethylaniline hydrochloride and the decomposition products of formic acid; the amount of tertiary amine formed is usually small, even when excess of the ethereal salt is employed. J. J. S.

The Hydrochlorides of Methylaniline and Dimethylaniline. By ROLAND SCHOLL and RICHARD ESCALES (*Ber.*, 1897, **30**, 3134—3137). —Methylaniline hydrochloride, which can readily be obtained crystalline by passing dry hydrogen chloride into a cooled ethereal solution of the base, deliquesces on exposure to the atmosphere, and is insoluble in ether and benzene, readily soluble in alcohol. *Dimethylaniline monhydrochloride*, NMe_2Ph,HCl, which separates as a white, crystalline mass on passing hydrogen chloride into the cooled base, melts at about 85—95° and rapidly deliquesces on exposure to the air. When it is treated with an excess of hydrogen chloride, the *dihydrochloride*, $NMe_2Ph,2HCl$ is formed, which melts at about 60—70°, and when heated at 65—75° is reconverted into the monhydrochloride. These salts can also be obtained by passing hydrogen chloride into an ethereal solution of the base. A. H.

Reduction of Metanitrodimethylparatoluidine. By JOHANNES PINNOW (*Ber.*, 1897, **30**, 3119—3122).—When metanitrodimethylparatoluidine is reduced, it not only yields the corresponding amido-compound, but also a substance containing chlorine, not yet isolated, and a solid base of high boiling point, which appears to be *metadimethylbenzimidazole*, $C_9H_{10}N_2$; the latter, which is also formed when metamidomethyltoluidine is heated with formic acid, boils at 301° (uncorr.) under a pressure of 780 mm., and crystallises in needles melting at 94·5—95·5°. The *hydrochloride*, $C_9H_{10}N_2,HCl$, crystallises with $1H_2O$ in needles and, after being dried, melts at 214—215° (uncorr.); the *picrate* crystallises in minute needles, and not in plates, as previously stated (Abstr., 1896, i, 161). The base is not acted on by nitrous acid and acetic anhydride, and, therefore, probably does not contain a primary or secondary amido-group.

Derivatives of benzimidazole have been obtained by the reduction of several other nitro-compounds, and the reaction is being further investigated. A. H.

Formation of Chains. XXIV. Benzylamine. XXV. Methylaniline. XXVI. Ethylaniline. By CARL A. BISCHOFF (*Ber.*, 1897, **30**, 3169—3173, 3174—3178, 3178—3180. Compare this vol., i, 73, 131).—The numbers in the following table give the approximate extent

in percentages of the theoretical maximum to which action takes place between the amines and ethylic salts there tabulated.

Ethylic salt.	Benzylamine.		Methylaniline.	Ethylaniline.	
	At 100°	At 120°	At 100°	At 100°	At 120°
Bromopropionate	98·0	99·4	91·0	78·7	95·5
Bromophenylacetate	59·5		69·1	46·5	
Bromobutyrate		94·4	65·4		66·3
Bromisobutyrate..........................		90·0	7·7		8·0
Bromisovalerate		87·7	0·0		8·1

The following new substances were prepared in the course of the investigation.

Ethylic benzylamidopropionate, $CH_2Ph\cdot NH\cdot CHMe\cdot COOEt$, is a colourless oil having a faint ammoniacal odour; it boils at 265—275°. *Ethylic benzylamidobutyrate*, $CH_2Ph\cdot NH\cdot CHEt\cdot COOEt$, boils at 275—285°. *Ethylic benzylamidoisovalerate*, $CH_2Ph\cdot NH\cdot CHPr^{\beta}\cdot COOEt$, boils at 170—175° under a pressure of 25 mm., and at 274—276° under atmospheric pressure; the first portion of the distillate consists of benzylamine carbonate. *Ethylic methylanilidopropionate*,

$$NMePh\cdot CHMe\cdot COOEt,$$

and *ethylic methylanilidobutyrate*, $NMePh\cdot CHEt\cdot COOEt$, are oils, and *ethyl methylanilidophenylacetate*, $NMePh\cdot CHPh\cdot COOEt$, crystallises from petroleum in needles, and melts at 72°. *a-Bromopropionylmethylanilide*, $NMePh\cdot CO\cdot CHMeBr$, separates from petroleum in triclinic crystals, and melts at 46°; *a-bromobutyrylmethylanilide*, $NMePh\cdot CO\cdot CHEtBr$, boils at 170—180° under a pressure of 10 mm. *a-Bromisobutyrylmethylanilide*, $NMePh\cdot CO\cdot CMe_2Br$, crystallises from petroleum and melts at 44°. *Ethylic ethylanilido-a-propionate*, $NEtPh\cdot CHMe\cdot COOEt$, boils at 268—270° under a pressure of 771 mm.; *Ethylic ethylanilido-a-butyrate*, $NEtPh\cdot CHEt\cdot COOEt$, boils at 273—276° under a pressure of 751 mm.

a-Bromopropionylethylanilide, $NEtPh\cdot CO\cdot CHMeBr$, and *a-bromobutyrylethylanilide*, $NEtPh\cdot CO\cdot CHEtBr$, are viscous oils; *a-bromisobutyrylethylanilide*, $NEtPh\cdot CO\cdot CMe_2Br$, melts at 80—80·5°. *a-Bromisovalerylethylanilide*, $NEtPh\cdot CO\cdot CHBr\cdot CHMe_2$, is a viscous oil, and boils at 148—165° under a pressure of 4 mm. M. O. F.

Formation of Chains. XXIII. Orthamidophenol and Paramidophenol. By CARL A. BISCHOFF (*Ber.*, 1897, 30, 2926—2930). —Orthamidophenol reacts with ethylic α-bromopropionate in presence of sodium sulphite, which is added to prevent oxidation, producing *methylphenomorpholone*, $C_6H_4{<}\begin{array}{l}NH\cdot CHMe\\ \quad\;\;\, |\\ O\text{——}CO\end{array}$, which crystallises in rhombic tablets melting at 109—111°, whilst ethylic α-bromobutyrate, under the same conditions, undergoes a different type of reaction, yielding *ethylic orthohydroxyanilidobutyrate*, $OH\cdot C_6H_4\cdot NH\cdot CHEt\cdot COOEt$, which melts at 81°. Ethylic α-bromisobutyrate reacts differently from either of the preceding, and forms *isobutyro-orthamidophenol*

[*orthamidophenylic isobutyrate*], $CHMe_2\cdot CO\cdot O\cdot C_6H_4\cdot NH_2$, which crystallises in asymmetric tablets and prisms melting at 112—115°.

Paramidophenol, on the other hand, only forms derivatives of a single type with these three brominated acids. *Ethylic parahydroxyanilidopropionic acid*, $OH\cdot C_6H_4\cdot NH\cdot CHMe\cdot COOEt$, formed from ethylic α-bromopropionate, melts at 86°; *ethylic parahydroxyanilidobutyrate* crystallises in colourless, lustrous needles, melting at 59·5°, whilst *ethylic parahydroxyanilido-isobutyrate*, which is apparently formed in two isomeric modifications, only one of which has been isolated, crystallises in lustrous, yellowish prisms melting at 91—91·5°. The isobutyric derivative is formed in the smallest quantity.

A. H.

Action of Formaldehyde on Paraphenetidine and on Paranisidine in Acid Solution. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1897, **21**, 395—396).—When paraphenetidine is treated with an excess of formaldehyde in the presence of strong hydrochloric acid, a *hydrochloride* is obtained which, on treatment with alkali, yields a *base*, $C_{18}H_{22}N_2O_2$, crystallising from alcohol in glistening plates and melting at 140°; it is practically insoluble in water and only sparingly soluble in ether. It yields two *hydrochlorides*, $C_{18}H_{22}N_2O_2,2HCl$, melting at 122°, and $C_{18}H_{22}N_2O_2,HCl$, melting at 193°. The *salicylate* of the base has physiological properties similar to those of cocaine.

Paranisidine, when treated in the same manner, yields two isomeric *bases*, $C_{16}H_{22}N_2O_2$. The one is more readily soluble in alcohol, crystallises in glistening plates melting at 122°, is but sparingly soluble in ether, and its *hydrochloride* melts at 210°. The second is sparingly soluble in alcohol, melts at 170°, and yields a *hydrochloride* melting at 112°.

J. J. S.

Derivatives of Tetramethylmetaphenylenediamine. By JOHANNES PINNOW and M. WEGNER (*Ber.*, 1897, **30**, 3110—3119).—Tetramethylmetaphenylenediamine is best prepared by the action of hydrobromic acid and methylic alcohol on phenylenediamine. *Amidotetramethylmetaphenylenediamine*, prepared by reducing the nitrosotetramethylmetaphenylenediamine described by Witt (Abstr., 1885, 782), is a colourless liquid which boils at 209·4° under a pressure of 112 mm., has a sp. gr. = 1·0203 at 22°/4°, and rapidly becomes dark coloured on exposure to the air. The *hydrochloride*, $C_{10}H_{17}N_3,2HCl$, melts at 164° (uncorr.), the *hydrobromide* at 179° (uncorr.), and the *hydriodide* at 175° (uncorr.); of the remaining salts may be mentioned the *sulphate*, which readily deliquesces, the *stannochloride*, which melts at 171°, and the *picrate*, which crystallises in small, feathery prisms and melts at 169° (uncorr.). The *acetyl* derivative crystallises in lustrous tablets, which melt at 85°, whereas the *benzoyl* derivative has not been obtained in the crystalline state, although it yields a crystalline *picrate* melting at 128° (uncorr.). *Tetramethyldiamidophenylcarbamide* forms small, microscopic needles, which melt at 173° (uncorr.). *Asymmetrical tetramethyldiamidocarbanilide* crystallises in lustrous prisms melting at 175° (uncorr.), whilst the corresponding *thiocarbanilide* forms compact crystals melting at 143° (uncorr.). *Tetramethyldiamidourethane* has not been obtained in the crystalline state, but it yields a

picrate, which crystallises in light yellow plates and melts at 167° (uncorr.). *Tetramethyldiamidobenzenesulphanilide*, $C_{16}H_{21}N_3SO_2$, crystallises in prisms melting at 84° and decomposes when boiled with water.

Acetic anhydride converts tetramethyltriamidobenzene into a crystalline compound which was only obtained in very small quantity and appears to be a benzimidoazole derivative. *Tetramethylmetaphenylenediamineazobenzenesulphonic acid* is a brownish-red mass which melts at 189° (uncorr.), and on reduction yields the tetramethyltriamidobenzene described above. The constitution of the triamido-base is shown by the fact that, on methylation, it is converted into the same hexamethyltriamidobenzene as is given by dimethyldiamido-aniline, the constitution of which is already known. The *hexamethyl* compound boils at 184° (corr.) under a pressure of 40 mm., and yields a crystalline *methiodide*, $C_6H_3N_3Me_6,3MeI + 2MeOH$, crystallising in needles, which melt and decompose at 164·5° (uncorr.). α-Diamidodimethylaniline boils at 195·5° (corr.) under a pressure of 40 mm. and yields a *hydrochloride* which melts at 225° (uncorr.), the corresponding hydrobromide melting at 207° (uncorr.) and the hydriodide at 190° (uncorr.). *Dinitrotetramethylmetaphenylenediamine* is formed when the tetramethyl compound is submitted to nitration by the method previously employed for dimethylaniline (Abstr., 1896, i, 427).

A. H.

Acylimido-ethers. By HENRY L. WHEELER, PERCY T. WALDEN and H. F. METCALF (*Amer. Chem. J.*, 1898, **20**, 64—76. Compare Abstr., 1897, i, 280).—The preparation of acylimido-ethers in an approximately pure state is in some cases attended with difficulty on account of the ease with which they react with water, in presence of acids, in one of two ways; either alcohol is separated and a diacylamide formed, or a monacylamide and an ethereal salt are produced. To what extent the acylimido-ethers decompose in the first case otherwise than indicated has not been fully investigated, but when acted on with ammonia they give acylamidines, which will form the subject matter of another paper. The imido-ether hydrochlorides were obtained by Pinner's well known method, and the free ethers were prepared according to Bushong's directions (Abstr., 1896, i, 546).

Benzimidomethylic ether, OMe·CPh⁚NH, boils at 96° under a pressure of 13 mm., and on standing deposits crystals of cyanophenine. The *picrate* forms heavy, lemon-yellow crystals melting at 163°.

Benzobenzimidomethylic ether, OMe·CPh⁚NBz, prepared by the action of benzoic chloride on the above imido-ether, is a colourless oil boiling at 210—212° (12 mm.); when treated with a little hydrochloric acid in alcoholic solution, dibenzamide is formed.

Carbethoxybenzimidomethylic ether, OMe·CPh⁚N·COOEt, obtained by the action of ethylic chlorocarbonate on benzimidomethylic ether, is a colourless oil boiling at 155° (14 mm.); hydrochloric acid converts it into benzoylurethane.

Ethyloxalylbenzimidomethylic ether, OMe·CPh⁚N·CO·COOEt, obtained from the above imido-ether and ethylic chloroxalate boils at 192° (14 mm.). On standing, or when boiled with water, it is converted into ethylic benzoate and oxamethane, and is decomposed by aqueous

ammonia into oxamide and methylic benzoate. The corresponding *ethyl ether* boils at 190—195° (11 mm.).

Benzimidoethylic ether distils at 101—102° (15 mm.); when treated with mercuric chloride in alcoholic solution, an additive product separates in colourless needles.

Acetobenzimidoethylic ether boils at 156° (17 mm.); when mixed with benzoic chloride and kept at 100—120°, tribenzamide separates. The corresponding *propionyl* compound is an oil boiling at 161—162° (17 mm.); when treated with hydrochloric acid, it is converted into *propionobenzamide*, which crystallises in needles or prisms and melts at 98°. The normal *butyryl* compound boils at 167° (16 mm.) and when treated in a similar manner yields *butyrobenzamide* in beautiful colourless prisms melting at 104—105°. The *benzoyl* compound, which separates in rhomboidal crystals melting at 65°, is converted by sulphuric acid into dibenzamide, whilst the action of benzoic chloride yields tribenzamide; as the latter reaction is analogous to that of the acyl chlorides on the isoanilides, in which case diacylanilides are formed, it indicates that in triacylamides all three acyl groups are attached to nitrogen.

Dibenzoethylamide, $NEtBz_2$, isomeric with benzobenzimidoethylic ether, is obtained by treating the sodium salt of ethylbenzamide with benzoic anhydride; it crystallises from alcohol in colourless prisms melting at 101—102°.

Benzimidopropylic ether is a colourless, pleasant smelling oil boiling at 232° under ordinary atmospheric pressure, or at 115·5° (12 mm.). The *hydrochloride* melts at 125°, giving off ethylic chloride and forming benzamide; the *picrate* crystallises in lemon-yellow prisms melting and decomposing at 261°.

Acetobenzimidopropylic ether, obtained by the action of acetic chloride on the imido-ether, is an oil boiling at 153° (13 mm.); on exposure to air it deposits acetobenzamide. The corresponding *benzoyl* compound boils at 231—232·5° (17 mm.) and gives dibenzamide on treatment with hydrochloric acid.

Benzimidoisobutylic ether boils without decomposition at 248—250° under atmospheric pressure, or at 117·5—120° (9 mm.).

Benzoylbenzimidoisobutylic ether melts at 54·5° and boils at 228—235° (15 mm.).

Phenylacetimidomethylic ether, $OMe\cdot C(C_7H_7)\colon NH$, is a pleasant smelling oil distilling at 114·5—115° (20 mm.). The *ethylic* ether boils at 116° (15 mm.).

Benzoylphenylacetimidoethylic ether, $OEt\cdot C(C_7H_7)\colon NBz$, boils at 215—216° (13 mm.) and readily decomposes into benzamide and phenylethylic acetate. A. W. C.

Influence of the Side Chain on the Velocity of Decomposition of Benzene Derivatives. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1897, 30, 2966—2975).—*Disubstituted benzene derivatives.*—The reaction between allylic bromide and the three toluidines has been studied and the following velocity constants obtained: ortho-toluidine, 54; meta-, 445, and para-, 96.

The action of dipropylamine on the three bromonitrobenzenes was

studied by heating the two substances together, without any solvent, for 45 minutes in nitrobenzene vapour. The numbers are: orthobromonitrobenzene, 88·8; meta-, 0, and para-, 21·7 per cent.

The author regards these as two phases of the same type of distribution of velocity constants, both of which are characterised by the preponderating influence of the meta side chain. In the first case, when the meta-position gives a maximum, the ortho gives a minimum, and in the second, when the meta gives a minimum, the ortho gives a maximum; in both, the para takes an intermediate position. The second type of distribution is met with in the action of allylic bromide on chloranilines, and also in the hydrolysis of the three tolylsuccinimides by sodium hydroxide at 25° (Miolatti and Lotti). The constants are, for the chloranilines, ortho, 9; meta, 23; para, 34; and for the tolylsuccinimides, ortho, 8558; meta, 10980; para, 1200. In both, the ortho-compound coincides with a minimum constant, and the para with a maximum, the meta being intermediate. The second phase of this second type, namely, where the para-position corresponds with a minimum and the ortho with a maximum, has not been met with as yet in any chemical reaction. The dissociation constants of the chloro- and hydroxy-benzoic acids (compare Ostwald) follow, however, the above order; in both cases, the constant for the ortho-acid is a maximum and for the para-, a minimum.

Tri-derivatives of Benzene.—Similar types are to be met with here, if we suppose that two of the three groups remain fixed and the third alone changes its position. For example, in the hydrolysis of the six xylylsuccinimides with sodium hydroxide, Miolatti and Lotti give the following constants: ortho-ortho, 1571; ortho-meta, 8147; ortho-para, 8653; meta-ortho, 8757; meta-meta, 11450; meta-para, 12700. In both sets, we have the first phase of the second type, namely, a maximum with the para-compound and a minimum with the ortho-.

In the action of allylic bromide on the six xylidines, the following numbers were obtained, [$Me_2 : NH_2 = 1:3:2$] 129, [1 : 2 : 3] 400, [1:3:4] 235; [1 : 4 : 3] 185, [1 : 3 : 5] 209, [1 : 2 : 4] 707. In both these sets we find a minimum in the ortho-position, but in the first set the maximum corresponds with the meta-, and in the second with the para-position.

Tetra-derivatives.—The action of allylic bromide on mesidine and cumidine gave the constant for mesidine = 115, and for cumidine = 174.

The author compares these results with the rules of orientation found by Körner, Griess, and others, when benzene and its derivatives are nitrated, chlorinated, &c. It is thought that all these results can only be explained by the adoption of both the diagonal and the Kekulé formula for benzene. J. J. S.

Action of Diazomethane on Nitrosobenzene. By HANS VON PECHMANN (*Ber.*, 1897, **30**, 2871—2879. Compare this vol., i, 75).—Further evidence is adduced in favour of regarding the compound obtained from diazomethane and nitrosobenzene as the *n*-phenyl ether of glyoxime. The substance is synthesised from formaldehyde and phenylhydroxylamine with the intermediate production of the com-

pound, $CH_2(NPh\cdot OH)_2$; it is also obtained from glyoxal and phenylhydroxylamine, and is resolved into these products under the influence of acids and of phenylhydrazine. Acetic anhydride converts it first into oxanilide, and subsequently into vinylidene oxanilide (this vol., i, 135).

Glyoxime *n*-phenyl ether is prepared by treating an ice-cold solution of nitrosobenzene (5 grams) in ether, with an ethereal solution of diazomethane obtained from nitrosomethylmethane (5 grams); the mother liquor of the first crop of crystals deposits a second fraction when concentrated and treated with petroleum, and the filtrate from this fraction contains phenylhydroxylamine and azoxybenzene. The most convenient method of preparation consists in treating a solution of phenylhydroxylamine with the hydrogen sodium sulphite compound of glyoxal, and acidifying the solution with acetic acid.

Glyoxime *n-parabromophenyl ether* is prepared from diazomethane and nitrosobromobenzene, and also by brominating the phenyl ether; it crystallises from hot, glacial acetic acid in yellow needles, and melts at 278°. Alcoholic potash converts it into *paradibromazoxybenzene*, which crystallises from alcohol in yellow leaflets, and melts at 172°.

Glyoxime *n*-phenyl ether is resolved into phenylhydroxylamine and glyoxal by phenylhydrazine, parabromophenylhydrazine, and asymmetric methylphenylhydrazine, which give rise to the respective osazones. Alcoholic potash converts it into azoxybenzene and aniline.

M. O. F.

Reduction Products of the Nitrated Dimethylanilines. By Emilio Noelting and Émile Fourneaux (*Ber.*, 1897, **30**, 2930—2947).—*Metanitrodimethylaniline hydrochloride*, $C_8H_{10}N_2O_2,HCl$, crystallises in colourless needles which are sparingly soluble in alcohol, the *hydrogen sulphate* in colourless plates, and the *picrate* in small, greenish-yellow needles.

Various products are obtained by the reduction of metanitrodimethylaniline, according to the reducing agent employed. *Metazoxydimethylaniline*, $O<\begin{matrix}N\cdot C_6H_3\cdot NMe_2\\ | \\ N\cdot C_6H_3\cdot NMe_2\end{matrix}$, formed by heating the nitro-compound with a concentrated solution of sodium methoxide in methylic alcohol, forms compact, orange-red crystals melting at 88—89°, and yields colourless, soluble salts with acids; of these, the *hydrochloride* crystallises in small, white needles, the *hydrogen sulphate* in colourless needles, and the *oxalate* in pale yellow needles; the *platinochloride* is a yellow, crystalline precipitate; the *picrate* crystallises in lustrous, red, pointed pyramids, and the *ferrocyanide* in pale yellow needles almost insoluble in water. The azoxy-compound is identical with that produced by the methylation of the metazoxyaniline, formed by the action of aqueous soda and zinc dust on nitraniline, and also with the hydrazoaniline described by Haarhaus (*Annalen*, **135**, 164). When its hydrobromide is boiled with methylic alcohol, or when the azoxy-compound itself is treated with methylic iodide in presence of an alkali, metazoxydimethylaniline is produced.

Metazoxydimethylaniline methiodide forms small, yellow crystals which melt and decompose at 190°.

Metazodimethylaniline, $N_2(C_6H_3\cdot NMe_2)_2$, which has previously been described by Lauth (Abstr., 1892, 1222) is best prepared by reducing the nitro-derivative with zinc dust and aqueous soda, and then reoxidising the hydrazo-derivative thus formed. It crystallises in red needles melting at 118°, and, with acids, yields coloured, sparingly soluble salts; of these, the *hydrochloride* crystallises in golden-yellow plates, and the *platinochloride* is an orange-coloured, crystalline powder; the *sulphate*, *oxalate*, *picrate*, and *ferrocyanide* are all yellow, crystalline substances. Metazodimethylaniline is also formed by the methylation of metazoaniline. The *methiodide* forms orange-yellow crystals which melt and decompose at 230°; the corresponding ammonium hydroxide, like that of the azoxy-derivative, is very unstable. *Metazoaniline*, obtained in the preparation of metazoxyaniline, crystallises in orange-yellow needles melting at 144°, and is identical with the compound described by Graeff (Abstr., 1885, 1127) as hydrazoaniline. The *hydrobromide* crystallises in plates which are readily soluble in water. *Metahydrazodimethylaniline*, $N_2H_2(C_6H_3\cdot NMe_2)_2$, crystallises in white needles melting at 99—100°, and oxidises very readily when moist. Tetramethyldiamidobenzidine, which has also been described by Lauth, can be obtained by the reduction of metazodimethylaniline with tin and alcoholic hydrogen chloride, or by the direct action of hydrochloric acid on the hydrazo-compound; it crystallises in colourless needles melting at 166·5—166°. An acid solution of the base gives an intense violet coloration with a nitrite. The *hydrochloride*, *sulphate*, and *oxalate* are all colourless, crystalline substances. The benzidine is accompanied by dimethylmetaphenylenediamine and a diphenyline derivative, the *hydrochloride* of which, $C_{16}H_{12}N_4,4HCl + 4H_2O$, crystallises in colourless needles. *Tetramethyldiamidobenzidine methiodide* crystallises in colourless needles, and yields a stable ammonium hydroxide. The benzidine compound is converted by methylation into the methiodide of *octomethyldiamidobenzidine*; the *dimethiodide* of this, $C_{12}H_6(NMe_2)_4,2MeI$, crystallises in long, colourless needles which melt and decompose at 190°; the *tetramethiodide* forms lustrous, white needles, and melts and decomposes at 205°. The free base, which has only been obtained in very small quantity, crystallises in needles melting at 176—178°. Tetramethyldiamidobenzidine readily forms colouring matters with diazo-salts, &c. *Monophenylazotetramethyldiamidobenzidine* forms orange-coloured needles melting at 220—221°, and dyes brown on a tannin mordant. *Diphenyldisazotetramethyldiamidobenzidine* is similar to the foregoing, but dyes a redder shade on tannin; the platinochloride forms reddish-brown crystals. The colouring matters formed with diazobenzenesulphonic acid are less powerful dyes; with nitrosodimethylaniline hydrochloride an indamine is formed; an azine has also been prepared which dyes cotton directly a bright bluish-violet. The colouring matters obtained from the isomeric diphenyline compound are similar in general character to the foregoing; the azines do not, however, dye unmordanted cotton.

Parazodimethylaniline, which is obtained in small amount by the reduction of the corresponding azoxy-compound, is identical with the compound obtained by the action of phenylhydrazine on nitrosodimethylaniline by O. Fischer and Wacker (Abstr., 1888, 1286). The authors were unable to obtain the compound described by Barbier and

Vignon (Abstr., 1888, 54) as being formed by heating an alcoholic solution of aniline and nitrosodimethylaniline. A. H.

Isomerism amongst the Oxidation Products of the Hydrazones. By GAETANO MINUNNI (*Gazzetta*, 1897, 27, ii, 215—235).—On oxidising metanitrobenzylidenephenylhydrazone suspended in ether by boiling it with amylic nitrite, a mixture of dimetanitrobenzylidenediphenylhydrotetrazone and dehydrometanitrobenzylidenephenylhydrazone crystallises out and is separated mechanically. *Diphenyldimetanitrobenzylidenehydrotetrazone*,

$$NO_2 \cdot C_6H_4 \cdot CH \colon N \cdot NPh \cdot NPh \cdot N \colon CH \cdot C_6H_4 \cdot NO_2,$$

which crystallises in thin, yellow needles, partially melts at 147—148° and then resolidifies, being converted into isodehydrometanitrobenzylidenephenylhydrazone; it is only sparingly soluble in cold acetic acid, alcohol or benzene, but soluble in chloroform, and turns blue with concentrated sulphuric acid. The isomeric *dehydrophenylmetanitrobenzylidenehydrazone*, $C_{26}H_{20}N_6O_4$, crystallises in minute, yellow needles, melting at 190—194°, and is sparingly soluble in alcohol, acetic acid, or chloroform. On heating the tetrazone to 154°, it changes into *isodehydrophenylmetanitrobenzylidenehydrazone*, $C_{26}H_{20}N_6O_4$, a yellow crystalline powder which melts at 244—245° without blackening, whereas the dehydro-compound blackens at that temperature; unlike its two isomerides, it gives no blue colour with concentrated sulphuric acid.

Phenylanisylidenehydrazone, when similarly oxidised with amylic nitrite, yields a mixture of diphenyldianisylidenehydrotetrazone and dehydrophenylanisylidenehydrazone, which may be separated by crystallisation from benzene and alcohol. *Diphenyldianisylidenehydrotetrazone*, $C_{28}H_{26}N_4O_6$, crystallises in yellow needles melting at 152°, and is also obtained in small yield by treating an ethereal solution of anisylidenephenylhydrazone with yellow mercuric oxide; the isomeric *dehydroanisylidenephenylhydrazone*, which melts at 190°, is yellow and crystalline, and is also obtained by heating the tetrazone at 155°.

Phenylcuminylidenehydrazone, when oxidised with amylic nitrite, yields a mixture of dicuminylidenediphenylhydrotetrazone and dehydrocuminylidenephenylhydrazone which can be separated by crystallisation from ether and alcohol. *Diphenylcuminylidenedihydrotetrazone*, $N_2Ph_2(N \colon CH \cdot C_6H_4Pr)_2$, crystallises in flattened, canary-yellow needles sparingly soluble in organic solvents; melting points were observed varying between 156° and 160°; this is due to its conversion into isodehydrophenylcuminylidenehydrazone, described below. *Dehydrophenylcuminylidenehydrazone*, $C_{32}H_{34}N_4$, is a crystalline, yellow powder melting at 151·5—152°, and dissolves readily in cold benzene or chloroform. On heating diphenyldicuminylidenehydrotetrazone to 165° and immediately cooling, it is converted into the isomeric *isodehydrophenylcuminylidenehydrazone*; this is a white, crystalline powder melting at 215—219°, very soluble in cold chloroform, and giving a reddish coloration with concentrated sulphuric acid, differing in this respect from its two isomerides which give a blue under similar conditions.

Phenylfurfurylidenehydrazone, on oxidation with amylic nitrite,

yields a mixture of diphenyldifurfurylidenehydrotetrazone and dehydrofurfurylidenephenylhydrazone, which can be separated by crystallisation from benzene. *Diphenylfurfurylidenedihydrotetrazone*, $N_2Ph_2(N\dot{:}CH\cdot C_4OH_3)_2$, crystallises in microscopic, yellow needles melting at 135—136° with decomposition; no isomeride could be isolated from the substance after fusion. *Dehydrophenylfurfurylidenehydrazone*, $C_{22}H_{18}N_4O_2$, crystallises in colourless needles melting at 155·5—161°; neither isomeride gives a characteristic colour with concentrated sulphuric acid. W. J. P.

Derivatives of α-Phenylbenzylhydrazine. By GAETANO MINUNNI. (*Gazzetta*, 1897, 27, ii, 235—244).—α-Phenylbenzylhydrazine combines readily with aldehydes; the hydrochloride of the hydrazine (1 mol.) and sodium acetate (1 mol.) are dissolved in alcohol, mixed, the sodium chloride filtered off, and the aldehyde (1 mol.) added to the filtrate. The following hydrazones were prepared in this way.

Phenylbenzylcuminylidenehydrazone, $C_6H_4Pr\cdot CH\dot{:}N\cdot NPh\cdot C_7H_7$, crystallises in white needles melting at 89—90°, and dissolves readily in organic solvents. *Phenylbenzylanisylidenehydrazone*,

$$OMe\cdot C_6H_4\cdot CH\dot{:}N\cdot NPh\cdot C_7H_7,$$

crystallises in yellowish needles melting at 135—136°. *Phenylbenzylmetanitrobenzylidenehydrazone* crystallises in beautiful, yellow needles melting at 140—141°. *Phenylbenzylfurfurylidenehydrazone*,

$$C_4H_3O\cdot CH\dot{:}N\cdot NPh\cdot C_7H_7,$$

separates in small, yellow crystals melting at 138°. *Phenylbenzylorthohydroxybenzylidenehydrazone* crystallises in white needles melting at 117·5°, and when boiled with acetic anhydride yields *phenylbenzylorthoacetoxybenzylidenehydrazone*, which crystallises in long, white needles melting at 141·5—142°.

Benzonitrile and α-phenylbenzylhydrazine do not react in benzene solution in presence of sodium, neither is a semicarbazide obtained on heating carbamide with α-phenylbenzylhydrazine at 165—170°, but instead a *substance* of the composition $C_{39}H_{34}N_4$, crystallising in nearly white needles melting at 108—109°; the study of this substance is being continued. W. J. P.

Constitution of Dehydrophenylbenzylidenehydrazone and its Conversion into Dibenzylidenediphenylhydrotetrazone. By GAETANO MINUNNI (*Gazzetta*, 1897, 27, ii, 244—262).—On heating dehydrophenylbenzylidenehydrazone with benzoic chloride for an hour on the water bath, pouring into water, and adding much potassium carbonate, *monobenzoyldehydrophenylbenzylidenehydrazone*,

$$CHPh\dot{:}N\cdot NPh\cdot CPh\dot{:}N\cdot NPhBz + \tfrac{1}{2}C_6H_6,$$

separates, and when crystallised from benzene is obtained as a crystalline powder melting at 172—173·5°; the benzene is but slowly evolved at 120—125°. On crystallising this substance from boiling alcohol, it is converted into an *isomeride*, $C_{26}H_{21}N_4Bz$, which crystallises in white needles melting at 187—188° with decomposition; both isomerides are hydrolysed by alcoholic potash with formation of benzoic acid and dehydrophenylbenzylidenehydrazone. The cause of the isomerism is unexplained. Dehydrophenylbenzylidenehydrazone yields an *acetyl* derivative, $C_{26}H_{21}N_4Ac$, which crystallises in colourless,

lustrous prisms melting at 124—125·5°, and is hydrolysed by alcoholic potash, yielding acetic acid and dehydrophenylbenzylidenehydrazone. The latter, therefore, contains one, and only one, imido-group, and has the constitution assigned to it above. Diphenyldibenzylidenehydrotetrazone gives no acetyl or benzoyl derivative, and consequently contains no imidogen group; its constitution is

$$CHPh⁚N·NPh·NPh·N⁚CHPh.$$

Dehydrophenylbenzylidenehydrazone should yield a nitroso-compound if the constitution assigned above be correct; on treating it, in acetic acid and chloroform solution, with sodium nitrite and hydrochloric acid, the *nitroso*-compound could not be isolated in a pure state, but diphenyldibenzylidenehydrotetrazone was separated. The hydrazone and the tetrazone are thus mutually convertible.

On the basis of these results, constitutions can be assigned to the substances described in the last abstract but one. Thus, diphenyldimetanitrobenzylidenehydrotetrazone melting at 148° has the constitution $NO_2·C_6H_4·CH⁚N·NPh·NPh·N⁚CH·C_6H_4·NO_2$, dehydrophenylmetanitrobenzylidenehydrazone is

$$NO_2·C_6H_4·CH⁚N·NPh·C(C_6H_4·NO_2)⁚N·NHPh,$$

whilst the isodehydro-compound possibly has the constitution

$$NHPh·N⁚C(C_6H_4·NO_2)·C(C_6H_4·NO_2)⁚N·NHPh.$$

W. J. P.

Action of Acid Chlorides on the Hydrotetrazones. By GAETANO MINUNNI (*Gazzetta*, 1897, **27**, ii, 277—292).—In the preceding abstracts, the author has shown that diphenyldibenzylidenehydrotetrazone gives no acidic derivative with acetic anhydride or benzoic chloride. On mixing the tetrazone with benzoic chloride, heating to 90°, cooling and treating with alcohol, the isomeric benzil-β-osazone melting at 221—223° is obtained; the tetrazone,

$$CHPh⁚N·NPh·NPh·N⁚CHPh,$$

is thus converted by isomeric change into the osazone,

$$NHPh·N⁚CPh·CPh⁚N·NHPh.$$

On distilling the osazone prepared either from the tetrazone or from benzil with benzoic chloride, the same triphenylosotriazone, $C_{20}H_{15}N_3$, melting at 120—121° is obtained. The tetrazone and the osazone react with benzoic chloride in a boiling salt water bath with production of a *substance* of the composition $(C_{14}H_{10}N)_x$, which crystallises in white scales melting at 211·5—212·5°. At 95—97°, the tetrazone gives with benzoic chloride a *substance* of the composition $C_{28}H_{20}N_2O_3$; it is a white powder melting at 183—187°.

The product of the action of benzoic chloride on the tetrazone at 90—95°, contains, besides benzil-β-osazone and the substance melting at 183—187°, a third *compound*, $C_{42}H_{34}N_4O_4$, which crystallises in white needles melting at 165—168°. W. J. P.

Oxidation of Formazyl Compounds derived from Acetyl, Benzoyl, and Methane. By EDGAR WEDEKIND (*Ber.*, 1897, **30**, 2993—2999).—It has been shown already (von Pechmann and Runge, Abstr., 1894, i, 240) that formazyl derivatives, NPh⁚N·CR⁚N·NHPh, yield tetrazolium bases, $CR\Big\langle\begin{matrix}N⁚NPh·OH\\ |\\ N·NPh\end{matrix}$, on oxidation. Some further

instances of this are now described. The method of oxidation adopted was to dissolve the formazyl compound in chloroform (or alcohol), add alcoholic hydrochloric acid, and pass in nitrous anhydride, when the chloride of the tetrazolium base, CN_4RPh_2Cl, separates.

Formazylic cyanide (R = CN; von Rothenburg, Abstr., 1894, i, 273) yields colourless *cyanodiphenyltetrazolium chloride*; this melts at 265—267°, is perhaps hydrolysed by hydrochloric acid to the carboxylic acid, and is reduced to formazylic cyanide by alkaline stannous chloride solution, and also by alkalis. Attempts were made to prepare formazylic bromide and chloride by the action of ethylic brom- and chlor-acetates on diazobenzene chloride in alkaline solution, but the products were found to contain no halogen; they were respectively yellowish-brown and dark-coloured powders, and melted at 198—200° and 177—178°. Formazyl methyl ketone (acetyl formazyl; R = Ac; Bamberger, Abstr., 1893, i, 159) is oxidised to *methylketodiphenyltetrazolium*, which could only be isolated in the form of its yellowish-white *platinochloride*; this melts and decomposes at 239°. The yield in this case is only about half of the theoretical. An impure *phenylhydrazone* of the *chloride*, decomposing at 112—115°, was also obtained. Formazyl phenyl ketone (benzoylformazyl; R = Bz; Bamberger and Witter, Abstr., 1894, i, 98) is oxidised to *phenylketodiphenyltetrazolium*, of which the yellowish-white *chloride* melts at 220—225°, and forms a reddish-brown *phenylhydrazone* melting and decomposing at 104—108°.

Formazylmethane (methylformazyl; R = Me; Bamberger and Müller, Abstr., 1894, i, 183) is not oxidised to a tetrazolium base when treated in the manner described; the product is orange coloured, melts at 232°, and contains chlorine, but it has not the properties of the salt of a base.

C. F. B.

Bismarck-brown. By Ernst Täuber and Franz Walder (*Ber.*, 1897, 30, 2899—2902. Compare this vol., i, 23).—In a dissertation published in 1895, Küchle expressed the view that triamidoazobenzene is but an inconsiderable constituent of Bismarck-brown, claiming on somewhat slender evidence that the colouring matter consists chiefly of phenylenedisazometaphenylenediamine. The authors find that this view is correct, comparison of the latter substance synthesised from diazotised metaphenylenediamine with the disazo-compound isolated from Bismarck-brown (*loc. cit.*) showing them to be identical.

Phenylenemetadisazometaphenylenediamine is prepared by slowly adding a solution of metabisdiazobenzene chloride to an ice-cold, aqueous solution of metaphenylenediamine and sodium carbonate which is well stirred; it separates from benzene in brownish-yellow crystals melting at 118°, and when recrystallised from a mixture of phenol and benzene melts at 136°.

Phenylenemetadisazometaphenylenediamine, is therefore, the chief constituent of Bismarck-brown, which contains also a small quantity of triamidoazobenzene, and a base which is insoluble in benzene.

M. O. F.

Absorption of the Violet Rays of Light by Unsaturated Ketones. By OTTO WALLACH (*Chem. Centr.*, 1897, i, 373—374; from *Nachr. der Kön. Gesell. Wiss. Göttingen*, 1896, Heft 4, 1—5).—The author has previously shown (compare *ibid.*, 1896, 73) that several ketones of the terpene series absorb light of certain wave-lengths; thus pulegone and eucarvone absorb the violet rays, whilst the isomeric ketones dihydrocarvone and carvone, transmit them unabsorbed. He now finds that several unsaturated ketonic compounds, such as mesityl oxide, phorone, and mono- and di-benzylideneacetone, also strongly absorb the violet rays; he draws the conclusion that the introduction of an ethylenic linking, adjacent to a carbonyl group, produces a greater absorptive power in a derivative than that possessed by its parent substance. If the carbon atoms on *both* sides of the carbonyl group are attached to the rest of the molecule by ethylenoid linkings, a still greater absorptive power is exhibited. Thus mesityl oxide shows a greater absorption of the violet rays than acetone; and phorone a greater absorption than mesityl oxide. The same holds in the case of acetone and the mono- and di-benzylideneacetones.

Substances which absorb the violet rays must appear yellow. A series of examples is adduced to show that compounds which contain the group $\colon C\cdot CO\cdot C$ are yellow, and that those which contain the group $\colon C\cdot CO\cdot C\colon$ are still more yellow; for instance, the condensation products of acetone and piperonal, $CH_2O_2\colon C_6H_3\cdot CH\colon CH\cdot CO\cdot CH_3$, and $CH_2O_2\colon C_6H_3\cdot CH\colon CH\cdot CO\cdot CH\colon CH\cdot C_6H_3\colon CH_2O_2$; styryloacetoacetic acid; and styrylformic acid. From the cyclic ketones containing the groups $CH_2\cdot CO$ or $CH_2\cdot CO\cdot CH_2$, yellow derivatives are obtained by replacing the two hydrogen atoms contained in either of these groups by a doubly-linked carbon atom (compare Abstr., 1896, i, 572). The groups, $C\colon CH\cdot CO$ and $C\colon CH\cdot CO\cdot CH\colon C$, are therefore chromophorous (compare Kesselkaul and Kostanecki, Abstr., 1896, i, 606; Friedländer and Löwy, Abstr., 1897, i, 32). Since isothujone and carvenone transmit the violet rays, they probably do not contain the group $C\colon CH\cdot CO$; whilst eucarvone probably contains it.

W. A. D.

Compounds formed by the action of Hydroxylamine on Ketones of the Type $CHR\colon CH\cdot CO\cdot CH\colon CHR$. By GAETANO MINUNNI (*Gazzetta*, 1897, 27, ii, 263—276).—On leaving a mixture of dibenzylideneacetone with hydroxylamine hydrochloride, suspended in alcohol at the ordinary temperature for 10 days, a *compound* is formed which crystallises in minute, white needles, melts at 142—144°, and seems to be a *dihydroisoxazole* derivative of the constitution

$$CHPr\colon CH\cdot C{<}{}^{CH_2}_{N\cdot O}{>}CHPh,$$

formed by intramolecular change of the oxime. The aqueous mother liquors contain small quantities of a *substance* melting at 164—165° which is very unstable, is soluble in alkalis, and is probably the oxime of dibenzylideneacetone.

On heating hydroxylamine acetate with dibenzylideneacetone in alcoholic solution and allowing the solution to evaporate spontaneously, the compound melting at 142° is obtained together with a *substance* of

the composition $C_{17}H_{18}N_2O_2$, which crystallises in beautiful, white prisms melting at 200·5—202°; it is probably formed by the interaction of the oxime with hydroxylamine.

On heating difurfurylideneacetone, hydroxylamine hydrochloride, and sodium acetate in alcoholic solution, filtering, and allowing the filtrate to evaporate spontaneously, a *substance* is obtained which crystallises in tufts of small prisms, melts at 162—164°, and has the composition $(C_4H_3O{\cdot}CH{:}CH_2)_2C{:}NOH,NH_2{\cdot}OH$; it seems to be an additive compound of the oxime with hydroxylamine. W. J. P.

Isomerism of Anils and Hydrazones. By ARTHUR R. HANTZSCH and ERNST VON HORNBOSTEL (*Ber.*, 1897, **30**, 3003—3009).—Möhlau and Hornbostel (Abstr., 1895, i, 140) have obtained two isomeric and interconvertible condensation products of ethylic acetoacetate with benzylamine. These may be regarded (1) as structurally isomeric, being respectively ethylic benzylimidobutyrate,

$$CH_2Ph{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOEt,$$

and benzylamidocrotonate, $CH_2Ph{\cdot}NH{\cdot}CMe{:}CH{\cdot}COOEt$; (2) as stereoisomeric ethylene derivatives, being the *cis* and *trans* forms of the second of these two substances; (3) as stereoisomeric nitrogen derivatives, being the *syn* and *anti* forms of the first substance. The authors have searched for similar cases of isomerism, but with only partial success; neither with ethylic benzoylacetate, acetophenone, benzophenone, benzophenone chloride, CPh_2Cl_2, nor anisyl phenyl ketone chloride can benzylamine be said with certainty to yield more than one condensation product. With ethylic acetoacetate, however, diphenylhydrazine does yield two interconvertible condensation products, although again with ethylic benzoylacetate only one product is obtained. If the second view of the condensation with benzylamine be adopted, then these two isomeric diphenylhydrazine derivatives must be regarded as hydrazides ($NPh_2{\cdot}NH{\cdot}CMe{:}CH{\cdot}COOEt$); it is probable, however, that they are hydrazones ($NPh_2{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOEt$), and if so that view must be rejected. The authors prefer to adopt the third view provisionally, whilst admitting that the first has almost equal justification.

Ethylic benzylimidophenylpropionate (or *benzylamidocinnamate*) melts at 68°. *Benzylimidoacetophenone* melts at 43—44°, and *benzylimidobenzophenone*, $CPh_2{:}N{\cdot}CH_2Ph$, at 64°; *benzylimidoanisyl phenyl ketone* forms an oil which possibly is a mixture of two isomerides.

Ethylic acetoacetate diphenylhydrazone is obtained first in the α-form; this melts at 120—135°, yielding a yellow liquid, the β-form, which does not solidify when cooled, although it is slowly reconverted into the α-form when kept at the ordinary temperature. *Ethylic benzoylacetate diphenylhydrazone* melts at 109—110°. C. F. B.

Preparation of Meta-, Chloro-, Bromo-, and Iodo-salicylic Acids. By TH. VAN WAVEREN (*Arch. Pharm.*, 1897, **235**, 566—570).—Monhalogen substituted salicylic acids are readily obtained by the oxidation of chloro-, bromo-, or iodo-salicin with potassium permanganate, and subsequent hydrolysis with hydrochloric acid; they prove to be identical with the known meta-acids. Metachlorosalicylic acid forms white needles melting at 172°, the corresponding bromo-acid melts at

165°, and the iodo-acid at 196°. The *barium*, *sodium*, *potassium*, and *silver* salts of the latter acid are described.

Hydroxysalicylic acid, $C_6H_2(OH)_2 \cdot COOH$ [$COOH:(OH)_2 = 1:2:5$], obtained by fusing iodosalicylic acid with caustic potash, separates from hot water in colourless crystals melting at 199°. Its solution is coloured blue by ferric chloride, turning to red on the addition of sodium hydrogen carbonate. It is readily converted into quinol, thus proving the meta-position of the second hydroxyl group and of the iodine atom in the iodosalicylic acid from which it is formed. (Compare Visser, this vol. i, 202). A. W. C.

Transformation of Unsaturated α-Hydroxy-acids into the Isomeric γ-Ketonic and α-Ketonic Acids.—By RUDOLPH FITTIG (*Annalen*, 1897, **299**, 1—49. Compare Abstr., 1897, i, 14).—[With MAX GINSBERG.]—Experimental evidence is adduced in support of the statement (Abstr., 1895, i, 533) that the so-called phenylhydroxycrotonic acid is identical with benzoylpropionic acid.

Benzoylbromopropionic acid, $COPh \cdot CHBr \cdot CH_2 \cdot COOH$, arises from the action of bromine on the unsaturated lactone produced by treating benzoylpropionic acid with acetic anhydride, the intermediate dibromo-compound losing hydrogen bromide under the influence of atmospheric moisture. It crystallises in the triclinic system; $a:b:c = 0{\cdot}64332:1:0{\cdot}5399$. $\alpha = 74° 42' 53''$. $\beta = 104° 25' 52''$. $\gamma = 92° 44' 15''$.

α-Hydroxy-γ-phenylcrotonic acid (Abstr., 1897, i, 14) crystallises from water in aggregates of needles, and melts at 137°. The *barium* and *calcium* salts are anhydrous; the *silver* salt dissolves with difficulty in cold water, and is decomposed when the liquid is boiled. The *amide* crystallises from boiling water in colourless leaflets, and melts at 141·5°.

[With NICOLAUS PETKOW.]—*βγ-Dibromo-α-hydroxy-γ-phenylbutyric acid*, $CHPhBr \cdot CHBr \cdot CH(OH) \cdot COOH$, is obtained by the action of bromine on α-hydroxyphenylcrotonic acid dissolved in chloroform; it separates from the solvent in small, prismatic crystals, and becomes violet at 151°, melts to a reddish-violet liquid, and evolves gas at 155°. It dissolves in hot water, yielding bromodihydroxyphenylbutyrolactone (E. Fischer and Stewart, Abstr., 1892, 1447).

α-Hydroxyphenylcrotonic acid yields βγ-phenylisocrotonic acid on reduction with sodium amalgam.

Benzylpyruvic (γ-phenyl-α-ketobutyric) acid, $CH_2Ph \cdot CH_2 \cdot CO \cdot COOH$, is produced when α-hydroxyphenylcrotonic acid is heated with 5 per cent. caustic soda during 2 hours; it dissolves with great readiness in ether, benzene, and chloroform, being sparingly soluble in carbon bisulphide, and almost insoluble in petroleum. It crystallises in lustrous plates, and melts at 46°; the aqueous solution deposits the acid in leaflets which also melt at 46° and contain $1\frac{1}{2}H_2O$. The *calcium* and *barium* salts crystallise in leaflets containing $1H_2O$, and the *silver* salt becomes brown when boiled with water. The *phenylhydrazone* crystallises from alcohol in prisms, and melts at 144—145°; the *amide* melts at 179—180°.

α-Hydroxy-γ-phenylbutyric acid, $CH_2Ph \cdot CH_2 \cdot CH(OH) \cdot COOH$, is obtained by reducing the foregoing acid in aqueous solution with 4

per cent. sodium amalgam, carbonic anhydride being passed through the liquid; it crystallises from a mixture of ether and petroleum in colourless leaflets, and melts at 104·5—105°. The *silver* salt is sensitive towards light, and is decomposed by boiling water.

[With MILTON FR. SCHAAK.]—α-Hydroxypentenoic acid (Abstr., 1897, i, 15) remains liquid at − 18°. The *calcium* salt contains $3H_2O$, the *zinc* salt $2\frac{1}{2}H_2O$, whilst the *barium* salt is anhydrous; the *silver* salt crystallises from warm water in slender needles.

βγ-Dibromo-α-hydroxyvaleric acid, CHMeBr·CHBr·CH(OH)·COOH, obtained by the action of bromine on α-hydroxypentenoic acid dissolved in chloroform, crystallises in needles, and when freshly prepared melts indefinitely at 60—79°; after remaining for 10 days in the desiccator, it melts at 104—105°.

Details of experiments are recorded, showing that during the conversion of α-hydroxypentonic acid into levulinic acid under the influence of dilute hydrochloric acid (*loc. cit.*), the hydroxylactone, $C_5H_8O_3$, is formed as an intermediate product. M. O. F.

Remarkable Conversion of an α-Ketonic Acid into the Corresponding α-Amido-acid. By EMIL ERLENMEYER, jun. (*Ber.*, 1897, **30**, 2976—2981).—The lactimide (m. p. 187°) obtained by the action of ammonia on α-benzamidocinnamic acid (Abstr., 1893, i, 582) is shown to be identical with the compound obtained by the action of ammonia on phenylpyruvic acid. When ammonia reacts with α-benzamidocinnamic acid, equivalent quantities of the lactimide and of benzamide are formed, thus proving that the lactimide cannot contain the benzoyl group. The acid, $C_{17}H_{17}NO_3$, which is formed when the lactimide is hydrolysed with hydrochloric acid or alkali, has the constitution CH_2Ph·CH(COOH)·NH·CO·CH_2Ph, since, when heated with concentrated hydrochloric acid, it yields phenylacetic acid and phenylalanine hydrochloride. Attempts are being made to synthesise the acid and thus prove its constitution. As the lactimide is readily obtained by the action of ammonia on the ethylic salt of the acid $C_{17}H_{17}NO_3$, it is regarded as the corresponding acid amide.

J. J. S.

Synthesis of Tyrosine. By EMIL ERLENMEYER, jun., and JOHN T. HALSEY (*Ber.*, 1897, **30**, 2981—2982).—Parahydroxybenzaldehyde, when warmed on the water bath with hippuric acid in the presence of acetic anhydride and fused sodium acetate, yields a yellow *lactimide* (compare Abstr., 1893, i, 580) which, when hydrolysed with sodium hydroxide, yields parahydroxy-α-benzamidocinnamic acid; this, when reduced with sodium amalgam, gives benzoyltyrosine, and the latter, when heated in sealed tubes with fuming hydrochloric acid, yields tyrosine. J. J. S.

Sinapic Acid. By JOHANNES GADAMER (*Arch. Pharm.*, 1897, **235**, 570—577. Compare Abstr., 1897, i, 360).—When acetylsinapic acid is treated with potassium permanganate, there is formed a crystalline substance melting at 167°, which is acetylsyringic acid (m. p. 181—183°), for although the melting point differs considerably, on hydrolysis with baryta water syringic acid is obtained crystallising

from water in long, nacreous crystals melting at 202°. The identity of the two substances was further proved by the preparation of the methylic and barium salts. From this it follows that, in sinapic acid, the methoxyl and hydroxyl groups are in the same position as in syringic acid, that is, a symmetrical one, where the hydroxyl is in the para-position relatively to the side chain.

On oxidising sinapic acid with chromic mixture, dimethoxyquinone is produced in glistening, golden yellow prisms melting at 249°, thus definitely proving the para-position of the hydroxyl group to the side chain, and as the methoxyl and hydroxyl groups together are to the side chain as [3 : 4 : 5] : 1, and, as already shown, the hydroxyl group is in position 4, then the methoxy-groups must occupy the positions 3 and 5, and the formula for sinapic acid is

$$COOH\cdot CH\colon CH\cdot C\begin{cases} CH\colon C(OMe) \\ CH\cdot C(OMe) \end{cases}C\cdot OH.$$

A. W. C.

β-Benzoylpropionic Acid. By Max Kugel (*Annalen*, 1897, **299**, 50—66. Compare this vol., i, 196).—The *phenylhydrazonehydrazide* of β-benzoylpropionic acid, $CPh(N\cdot NHPh)\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot NHPh$, obtained by heating the acid with phenylhydrazine on the water bath, crystallises from alcohol in prisms, and melts at 195°. The solution in concentrated sulphuric acid becomes violet with ferric chloride. The *anhydride*, $CPh\begin{cases} CH_2\cdot CH_2 \\ N—NPh \end{cases}CO$, is produced along with it, and separated by means of its greater solubility in alcohol, from which it crystallises in slender needles melting at 98—99°.

The lactone obtained on heating benzoylpropionic acid with acetic anhydride undergoes oxidation when the alcoholic solution is boiled with ferric chloride; the *compound*, $C_{20}H_{12}O_4$, separates from the liquid in lustrous, dark red crystals having a bluish reflex; after crystallisation from boiling xylene, it melts at 135°. *Diphenacylfumaric acid*, $COPh\cdot CH_2\cdot C(COOH)\colon C(COOH)\cdot CH_2\cdot COPh$, which is probably the compound obtained by the action of alcoholic potash on the foregoing oxidation product, crystallises from ether in yellowish prisms, and, without melting, passes into the compound, $C_{20}H_{12}O_4$, from which it is produced. The *silver* salt is insoluble in alcohol, ether, and water. The *compound*, $C_{20}H_{12}O_4$, isomeric with the red oxidation product already mentioned, is obtained by heating diphenacylfumaric acid with glacial acetic acid; it crystallises in slender, yellow prisms, and sublimes without fusion when heated. It is insoluble in ether and light petroleum, and sparingly soluble in boiling alcohol and glacial acetic acid; chloroform, boiling xylene, and boiling benzene dissolve it, however, forming solutions which exhibit a beautiful greenish fluorescence. The solution in concentrated sulphuric acid is brownish-red.

The *compound*, $C_{20}H_{14}O_3$, obtained by heating β-benzoylpropionic acid with benzoic chloride for 12 hours on the water bath, crystallises from dilute alcohol in slender prisms, and melts at 191—192°

Methylic benzoylpropionate melts at 18—20·5°, and boils at 187—187·5° under a pressure of 30 mm. The *ethylic* salt melts at 18—19·5°, and boils at 192·5° under a pressure of 33 mm.; when heated with alcoholic ammonia at 100° during 5—6 hours, it does not yield the amide, but

gives rise to two other nitrogenous compounds. The *compound*, $C_{10}H_9NO$, crystallises from alcohol in lustrous, orange prisms; it gradually becomes red when heated, darkens at 220—225°, and melts at 233°. The *compound*, $C_{10}H_7NO$, crystallises in yellowish-green leaflets with bronze reflex, appearing bluish under the microscope; it crystallises from aniline, and sublimes when strongly heated. A third substance of uncertain composition is separated from the red mother liquor on dilution with water. M. O. F.

Action of Hübl's Reagent on Tannic Acids and on Tannin Extracts. By CARL BOETTINGER (*Chem. Zeit.*, 1897, **21**, 460—461). —In previous communications (this vol., i, 30, 87), it has been shown that the acetyl derivatives of gallic and tannic acids give no "iodine number," whereas the free acids react with Hübl's reagent, but the "iodine number" varies with the amount and concentration of the iodine solution. Further experiments with tannic acids of different origin, oak bark, oak wood, and pine wood, and of their acetyl derivatives, confirm the former experiments. The action of Hübl's reagent on the following extracts has also been studied: Sumach, 165; algarobilla, 114; oak bark, 106; pine bark, 99; oak wood, 29; valonia, 153; quebracho, 188; terra japonica, 202; catechu pegu, 164; canaigre, 119. The numbers give the mean "iodine numbers." J. J. S.

Optical Behaviour of Tannin. By PAUL WALDEN (*Ber.*, 1897, **30**, 3151—3156. Compare Schiff, Abstr., 1896, i, 370).—The optical activity of commercial tannin has led H. Schiff to discuss a formula by which the substance is represented as containing an asymmetric carbon atom. The author's experiments, however, show that the tannin at present obtainable is not only a mixture, but also varies in composition; application of its optical behaviour to the question of its structure is, therefore, inadmissible.

It is suggested that the comparatively high optical activity of commercial tannin may be due to the exaggeration of the rotatory power of a small proportion of active impurity by the tannin itself.

M. O. F.

Orthodinitrocyanodibenzyl. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1897, **30**, 3017—3022).—This substance (Bamberger, Abstr., 1887, 131) is best obtained by dissolving powdered potassium cyanide (10·7 grams) in boiling methylic alcohol (260 c.c.), adding orthonitrobenzylic chloride (26 grams) and boiling for ¾ hour; the alcohol is then distilled off, the residue heated with water, and the oil, which solidifies after a while, recrystallised from a mixture of acetic acid (20 c.c.) and alcohol (5 c.c.); the substance is then pure enough for further use. When it is boiled for 1½ hours with a mixture of equal volumes of hydrobromic acid (sp. gr. = 1·47) and acetic acid, it is hydrolysed to *orthodinitrodibenzyl-α-carboxylic acid*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH(COOH)\cdot C_6H_4\cdot NO_2$, which melts at 170°. When this is reduced with ferrous hydroxide, or when orthodinitrocyanodibenzyl is heated with alcoholic ammonia at 100°, a yellow monacid *base*, $C_{15}H_{10}N_2$, melting at 342—343°, is obtained; the yellow *hydrochloride* melts at about 280°, and the yellowish-white *monacetyl* derivative at 185°; a yellow *mononitro*-derivative

was also obtained; it remained unmelted at 290°. This base is possibly

$$C_6H_4<\begin{matrix}CH:C\cdot C_6H_4\\ \quad | \quad | \\ N{=\!=}C\cdot NH\end{matrix} \quad \text{or} \quad C_6H_4<\begin{matrix}CH:C\cdot C_6H_4\\ \quad | \quad | \\ NH\cdot C:N\end{matrix}$$

and its formation has some analogy with the condensations observed by the author (Abstr., 1894, i, 603), and Reissert (Abstr., 1893, i, 687; 1894, i, 626). C. F. B.

Oxidation of Paranitrotoluenesulphonic Acid. By Arthur G. Green and André R. Wahl (*Ber.*, 1897, **30**, 3097—3101. Compare Ris and Simon, this vol., i, 143).—4 : 4′-dinitrodibenzyl-2 : 2′-disulphonic acid, $C_2H_4[C_6H_3(NO_2)\cdot SO_3H]_2$, is most readily obtained by the oxidation of sodium nitrotoluenesulphonate with sodium hypochlorite. The sodium salt (100 grams) is dissolved in water (1 litre) and added to a 30 per cent. caustic soda solution (500 c.c.), the hypochlorite solution (220 c.c. of solution containing 7 per cent. of active chlorine) is slowly run in, while the temperature is kept at 40—50° and the mixture rapidly stirred. In this reaction, it is necessary to add the hypochlorite gradually, so that no colour is developed. The mixture is still kept well stirred after the addition of the hypochlorite, and is tested from time to time with potassium iodide starch paper; when the iodide reaction becomes faint, the mixture is cooled and poured into 2 litres of cold water. The sparingly soluble sodium salt is then collected, washed with sodium chloride solution, and freed from a small quantity of dinitrostilbenedisulphonic acid by dissolving it in water and adding cold potassium permanganate solution. The free acid crystallises in colourless plates; when dissolved in cold caustic soda solution and then treated with a reducing agent, it does not yield a red coloration, whilst the corresponding stilbene derivative does give a colour; from this the authors conclude that Ris and Simon's acid must have contained a small quantity of the latter. It is also stated that this acid is identical with Bender's acid (Abstr., 1895, i, 287).

4 : 4′-dinitrostilbene-2 : 2′-disulphonic acid is obtained by a somewhat similar process. The sodium nitrotoluenesulphonate is dissolved in 2 litres of water, sodium hydroxide added, and then 500 c.c. of the sodium hypochlorite run in, the temperature being kept at 50° until all trace of hypochlorite has disappeared; on cooling, the sodium salt of the sulphonic acid crystallises out. The *free acid* crystallises in colourless needles, and is readily soluble in water. The *alkali* salts are readily soluble in hot water, moderately in cold, but almost insoluble in saline or alkaline solutions. The *aniline* and *phenylhydrazine* salts of both acids are colourless and very sparingly soluble. When sodium dinitrostilbenedisulphonate is oxidised with cold potassium permanganate, the chief product is sodium paranitrobenzaldehydorthosulphonate. J. J. S.

A Colouring Matter from Anhydrobisdiketohydrindene. By Carl T. Liebermann (*Ber.*, 1897, **30**, 3137—3144).—Anhydrobisdiketohydrindene, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C:C<\begin{matrix}C_6H_4\\CH\end{matrix}>C\cdot OH$, readily yields blue colouring matters with bases, condensation taking place between molecular proportions of the two constituents, with elimination of the elements of water. These compounds closely resemble the correspond-

ing colouring matters obtained from cœrulignone, which, however, are formed from 2 mols. of the base. Colouring matters have been thus obtained from aniline, toluidine, ψ-cumidine, parachlor- and parabromaniline, metamidobenzoic acid, α- and β-naphthylamine, metamidophenol, amidothymol, paranisidine, sodium sulphanilate orthotolylenediamine, paraphenylenediamine, paradiamidodiphenylmethane, and others, whilst no reaction is given by secondary or tertiary amido-compounds. The same substances may be obtained, but in much smaller yield, from diketohydrindene itself, which is probably first converted into the anhydro-compound. They are decomposed into their constituents when heated with hydrochloric acid, and are insoluble in dilute alkalis, but soluble in aqueous alkalis on boiling; and readily in alcoholic solutions of the alkalis.

Anhydrobisdiketohydrindeneparatoluidide, $C_{18}H_{10}O_2{:}N{\cdot}C_6H_4Me$, crystallises in needles which have a dark metallic lustre and form an orange-red solution in concentrated sulphuric acid. The other compounds are very like this in all their properties. No analogous compounds have been obtained from any other of the derivatives of diketohydrindene. With paratoluidine, phenyldiketohydrindene yields a *toluidide*, $C_6H_4<\genfrac{}{}{0pt}{}{\text{—CO—}}{C(N{\cdot}C_7H_7)}>CHPh$, which melts at 244°. A. H.

3 : 4-Dihydroxycinnamylidenecumaranone. By R. HALLER and STANISLAUS VON KOSTANECKI (*Ber.*, 1897, **30**, 2947—2952).—Compounds containing the chromophore, $CO{\cdot}C{:}C{\cdot}C{:}C$, have, as a rule, a redder shade than those containing the simpler group $CO{\cdot}C{:}C$. A substance of the former class, which is capable of dyeing mordanted cloth, is 3 : 4-*dihydroxycinnamylidenecumaranone*,

$$C_6H_2(OH)_2<\genfrac{}{}{0pt}{}{O—}{CO}>C{:}CH{\cdot}CH{:}CHPh.$$

this, which is obtained when cinnamaldehyde is treated with 3 : 4-dihydroxycumaranone in presence of dilute aqueous soda, crystallises in brownish-yellow plates or needles and yields a magenta-red coloured solution in sulphuric acid. With alumina mordants, it produces a slightly redder shade than the corresponding benzylidene derivative; it moreover gives a violet solution with alkalis, whereas the benzylidene-compound yields a red solution. *Diacetylcinnamylidenecumaranone*, crystallises in long, yellow needles melting at 176°, and decomposes on exposure to light. *Diethoxycinnamylidenecumaranone* crystallises in tufts of yellow needles melting at 123°. A. H.

Oxidation of Naphthalene with Permanganate. By JOHN PROCHÁZKA (*Ber.*, 1897, **30**, 3108—3109. Compare Henriques, Abstr., 1888, 842).—Naphthalene suspended in hot water and well agitated by the aid of an automatic stirrer, is readily oxidised at 100° by permanganate solution to phthalonic acid; this, in its turn, can be oxidised by manganese peroxide and acid to phthalic acid. Seventeen grams of phthalic acid were obtained with 100 grams of commercial permanganate. The unoxidised naphthalene can readily be recovered. J. J. S.

Ethereal Oil of Angostura Bark. By HEINRICH BECKURTS and JULIUS TROEGER (*Arch. Pharm.*, 1897, **235**, 634—640. Compare this vol., i, 37).—The authors have previously shown that when this crude left-handed oil is treated with acetic anhydride, it yields a right-handed terpene (18° in 100 mm. tube), which they called galipene. If phosphoric anhydride is used instead of acetic anhydride, inversion does not take place, and the terpene formed is of a clear green colour, and has the same boiling point as galipene, but is lævorotatory (rotation = $-10°$ in 100 mm. tube).

The fraction of crude oil boiling between 260° and 270°, when treated with phosphoric anhydride, gives an inactive sesquiterpene of a bluish-green colour, boiling at 256—260°.

When the right-handed terpene (galipene) is treated with a mixture of water, glacial acetic acid, and sulphuric acid, the elements of water are not directly added on to the terpene, but inversion takes place, and an inactive terpene is formed: whereas the raw angostura oil, under similar conditions, yields a second right-handed terpene (rotation = $+8{\cdot}5°$ in 100 mm. tube). Neither this terpene nor the left-handed and the inactive varieties give additive products when treated with glacial acetic acid and hydrogen chloride or bromide, thus differing from the so-called galipene. The authors are unable to account for this difference in behaviour, but are continuing the investigation with larger amounts of material. A. W. C.

Ethereal Oils. By EDUARD GILDEMEISTER and KARL STEPHAN (*Arch. Pharm.*, 1897, **235**, 582—592).—*Mandarin oil*, from *Citrus madurensis, Loureiro*, has a sp. gr. = 0·855 at 15°, and rotatory power $a_D = +69° 54'$ at 16°. It distils almost completely between 175° and 179°, and consists for the most part of right-handed limonene. The residue from the distillation, of which large amounts are now being worked up, appears to contain citral and citronellal.

Culilawan oil, from *Cinnamomum Culilawan*, has a sp. gr. = 1·051, and is soluble to a clear solution in three parts of alcohol; it contains from 61—62 per cent. of eugenol, together with small amounts of methyleugenol, and a substance boiling at 100—125° (10 mm.), the constitution of which has not been definitely decided.

Rosemary oil contains pinene (right and left-handed) as a normal constituent, and also inactive camphene.

Oil from the berries of Schinus molle, L. has a sp. gr. = 0·8505, rotatory power $a_D = +46° 4'$ at 17°, and, with sodium nitrite and acetic acid, gives an intense phellandrene reaction. It consists of about half a per cent. of pinene, phellandrene (right mixed with a little left-handed) and carvacrol, not thymol, as Spica (*Gazzetta*, 1884, **14**, 204) has stated. A. W. C.

Salicin and its Derivatives. By ERNST A. SCHMIDT (*Arch. Pharm.*, 1897, **235**, 536—544).—This is a summary of the results obtained by Visser and van Waveren (following abstracts and this vol., i, 196). E. W. W.

Halogen-substituted Compounds of Salicin and its Derivatives. By H. L. VISSER (*Arch. Pharm.*, 1897, **235**, 544—560).—See preceding abstract. Iodine does not act on salicin directly, but the

moniodo-derivative is obtained when chloride of iodine acts on an aqueous solution of salicin. Chlorosalicin melts at 154°, bromosalicin at 170°, and iodosalicin at 192°. These derivatives all crystallise in fine, white needles containing $2H_2O$, form red solutions in concentrated sulphuric acid, but give no reaction with ferric chloride. By the action of acetic anhydride, tetracetyl derivatives are formed; *tetracetylchlorosalicin* melts at 142°, *tetracetylbromosalicin* at 148°, and *tetracetyliodosalicin* at 119°. With emulsin, these compounds yield monhalogen derivatives of saligenin, and they give a blue coloration with ferric chloride. Chlorosaligenin melts at 93°, bromosaligenin at 113°, and iodosaligenin at 138°; attempts to obtain these compounds by the direct action of the halogen on saligenin failed, except in the case of the iodine derivative. When bromine acts on saligenin in alcoholic solution, tribromophenol is produced, and when bromine is added to an aqueous solution of saligenin made alkaline by sodium hydroxide, tribromosaligenin is formed as well as tribromophenol, whilst iodine added to an aqueous alkaline solution of saligenin gives iodosaligenin or di-iodosaligenin, according to the conditions. The monhalogen derivatives of saligenin, on oxidation with chromic mixture, yield the corresponding derivatives of salicylaldehyde and salicylic acid, and these are easily separated by distillation with steam. *Chlorosalicylaldehyde* melts at 99°, *bromosalicylaldehyde* at 104°, and *iodosalicylaldehyde* at 102°; chlorosalicylic acid at 167°, bromosalicylic acid at 164°, and iodosalicylic acid at 196°; these substituted aldehydes and acids give bluish violet colorations with ferric chloride in alcoholic solution.

[With Th. van Waveren.]—With hydroxylamine, the aldehydes form the corresponding aldoximes of which the chlorine compound melts at 122°, the bromine at 129°, and the iodine at 135°; by boiling with acetic anhydride, the aldoximes yield monacetyl-substituted derivatives of the corresponding nitrile. Chlorosalicylic acid is a meta-compound [COOH : OH : Cl = 1 : 2 : 5], for its melting point and the properties of its barium and silver salts are identical with those of the acid prepared by Hasse (Abstr., 1878, 416) and Varnholt (*J. pr. Chem.*, **36**, 16) from parachlorophenol. The chlorine in monochlorosalicylaldehyde is also in the meta-position, for this substance can be converted into the same monochlorosalicylic acid by means of its oxime. Similarly, chlorosalicin is a meta-compound, as the glucoside of chlorosalicylic acid prepared from it is decomposed into glucose and metachlorosalicylic acid. The identity of bromosalicylic acid with the meta-acid obtained by Hübner and Brencken (this Journal, 1873, 756) by direct bromination of salicylic acid indicates also the meta-composition of the bromine derivatives. E. W. W.

Helicin. By Th. van Waveren (*Arch. Pharm.*, 1897, **235**, 561—566).—By the oxidation of chloro-, bromo- or iodosalicin with nitric acid, it was hoped that the corresponding halcgenated helicins would be obtained, instead of which dihalogen substitution products of helicoidin, $C_{26}H_{32}X_2O_{14}$ (X = Cl,Br,I) are produced.

Bromohelicin, $C_{13}H_{15}BrO_7$, may be obtained, by modifying the action of nitric acid on bromosalicin, as white needles melting at 160°. Sulphuric acid hydrolyses it, with production of glucose and metabromo-

salicylaldehyde. This same substance mixed with bromohelicoidin or a polymerisation product is formed by the direct action of bromine on helicin.

Chlorohelicin, prepared by the action of chlorine on helicin, forms white needles melting at 166°, easily soluble in hot alcohol and water, and yielding glucose and metachlorosalicylaldehyde on hydrolysis, for which reason the author proposes the following formula for chloro- or bromo-helicin, where X = Cl,Br,

$$\begin{array}{l} CX\cdot CH{:}C\cdot COH \\ \| \qquad\qquad\ | \\ CH\cdot CH{:}C\cdot O\cdot C_6H_{11}O_5 \end{array}.$$

Iodohelicin could not be obtained by the action of nitric acid on iodosalicin, or of iodine chloride on helicin. A. W. C.

The Glucoside of Saponaria Rubra. By W. von Schulz (*Chem. Centr.*, 1897, i, 302 and 446; from *Pharm. Zeit. Rüss.*, **35**, 817—821, 833—839, 849—853).—Saporubrin, the active principle of *Saponaria rubra*, was first isolated by Kobert and Pachtorukow; details of the method employed are given. It must be distinguished from the sapotoxin of quillaja-bark, which it closely resembles. It is an amorphous powder, with a neutral reaction, and a taste which is at first cool, but becomes burning. Its aqueous solution gives a lather, and evolves carbonic anhydride; it is sparingly soluble in alcohol, but insoluble in the ordinary organic solvents. Concentrated sulphuric acid produces a reddish-brown coloration, which changes in the air, or on the addition of a drop of water, to a reddish-violet; this becomes emerald-green on adding potassium dichromate. Ferric chloride and alcoholic sulphuric acid produce a greenish-blue coloration. Barium hydroxide gives a white precipitate insoluble in water. Saporubrin rapidly reduces solutions of potassium permanganate and silver nitrate. It is optically active; $[\alpha]_D = -5{\cdot}44$. Its constitution is expressed by the formula $(C_{18}H_{28}O_{10})_4$. The *benzoyl* derivative, $(C_{18}H_{25}O_{10}Bz_3)_4$, melts at 208—210°.

The hydrolysis of saporubrin, with dilute sulphuric acid, gave varying amounts of sapogenin and glucose, according to the temperature; *sapogenins* having the formulæ $C_{17}H_{25}O_6$, $C_{18}H_{27}O_6$, $C_{18}H_{27}O_4$, $C_{14}H_{22}O_2$, were obtained, molecular weight determinations showing that these formulæ represent the molecular constitution of the substances. The *sapogenin* $C_{14}H_{22}O_2$ crystallises in microscopic needles, and melts at 248—250°; it is insoluble in water, easily soluble in alcohol, and soluble in ether, chloroform, methylic alcohol and glacial acetic acid. When freshly prepared, it dissolves in dilute alkalis. The *sugar* separated by the hydrolysis of saporubrin is not fermentable by yeast, and has $[\alpha]_D = +23{\cdot}67$; its *glucosazone* melts at 165—170°.

The root of *Saponaria rubra* contains 3·45 per cent. of saporubrin. From its empirical formula, saporubrin appears to be a methylsapotoxin, and closely resembles the sapotoxins of *Agrostemma*, quillaja, *Sapindus* and *Saponaria alba*. An injection into the veins of dogs and cats of 2 milligrams of saporubrin per kilogram of body weight causes death. Taken inwardly, it causes vomiting; on being injected, it produces rapid nervous and muscular paralysis. It shows the property characteristic of the saponins of dissolving the red blood-corpuscles.

W. A. D.

Some New Cuprammonium Compounds. By Icilio Guareschi (*Chem. Centr.*, 1897, i, 368; from *Estr. d. Accad. Tor.*, **32**). The author describes the preparation of a series of crystalline compounds of ammonia with the copper salts of the cyanhydropyridine derivatives dealt with in a former paper (Abstr., 1897, i, 168). Bluish-violet crystals of the *cuprammonium* derivative of cyanomethylglutaconimide, $(C_7H_5N_2O_2)_2Cu,4NH_3,2H_2O$, are obtained on adding copper sulphate to a solution of ammonium cyanomethylglutaconimide in aqueous ammonia; its composition is not altered by exposing it, in a vacuum, over calcium chloride. It is insoluble in cold water, but is decomposed by boiling water into ammonia, cupric oxide, and ammonium cyanomethylglutaconimide. At 100—125°, it loses water and is converted into a green *compound*, $(C_7H_5N_2O_2)_2Cu,2NH_3$. The *cuprammonium* derivative of methylcyanomethylglutaconimide,

$$(C_8H_8N_2O_2)_2Cu,4NH_3,4H_2O,$$

crystallises from ammonia, and on being dried in a desiccator loses all its contained water. From ethylcyanomethylglutaconimide a *derivative*, $(C_9H_9N_2O_2)_2Cu,4NH_3$, is obtained which is insoluble in water; on being heated, it loses $3NH_3$ at 180°, whilst the fourth molecule is only given up when the salt decomposes.

Benzylacetoacetamide, $CH_2Ph\cdot CHAc\cdot CO\cdot NH_2$, obtained by treating ethylic benzylacetoacetate with ammonia, melts at 149—150°, and is converted by ammonia and ethylic cyanacetate into *benzylcyanomethylglutaconimide*, $\begin{array}{l} CMe{=\!=}C(CN)\cdot CO \\ | \qquad\qquad\qquad\quad | \\ CH(C_7H_7)\cdot C(OH){:}N \end{array}$; this yields a *cuprammonium* derivative, $(C_{14}H_{11}N_2O_2)_2Cu,4NH_3,2H_2O$, which crystallises in blue needles, and is converted at 110° into $(C_{14}H_{11}N_2O_2)_2Cu,2NH_3$. The *cuprammonium* derivative of cyanophenylglutaconimide,

$$(C_{12}H_7N_2O_2)_2Cu,4NH_3,$$

is a blue, crystalline powder; it loses $2NH_3$ at 180°, and is nearly insoluble in ammonia and in water.

The author points out that those of the salts which are anhydrous are the most stable. All the substances described contain $4NH_3$; to explain this, the presence of the group $(NH_3)_2{:}Cu{:}(NH_3)_2$ is assumed.

W. A. D.

Bromination of 1-Ethoxyquinoline. By Adolph Claus and Hans Howitz (*J. pr. Chem.*, 1897, [ii], **56**, 390—392).—When 1-ethoxyquinoline (1 mol.) is treated with bromine (1 mol.) in acetic acid solution at the ordinary temperature, the dibromo-derivative is not formed. When the product is poured into water, 3 : 4-dibromo-1-hydroxyquinoline, melting at 196°, separates; whilst from the mother liquor, sodium acetate precipitates 4-*bromo*-1-*ethoxyquinoline*, and unchanged 1-ethoxyquinoline remains in solution. The bromethoxyquinoline melts at 55°; it forms a yellowish-red *platinochloride*, with H_2O, which melts and decomposes at 218—220°, and is hydrolysed by hydrochloric acid at 180° yielding 4-bromo-1-hydroxyquinoline melting at 124°.

1-Ethoxyquinoline, when treated with hydrogen bromide in ethereal solution, yields a hygroscopic *hydrobromide*, which melts and decomposes at 222—223°; when this (1 mol.) is heated with bromine (1 mol.)

in chloroform solution, it yields a *dibromide* additive product. Boiling with water converts this into 4-bromo-1-ethoxyquinoline and resinous substances; heating at 200° converts it into 1-hydroxyquinoline and the 4-bromo- and 3 : 4-dibromo-derivatives of this. C. F. B.

Action of Sulphur Chloride on Aromatic Amines. By ALBERT EDINGER (*J. pr. Chem.*, 1897, [ii], **56**, 273—282).—When 1-methylquinoline is mixed gradually with three times its weight of sulphur chloride, S_2Cl_2, the mixture being cooled with ice at first, but afterwards heated for several hours at 160—170°, a crystalline substance may be obtained from the product by extracting this with dilute hydrochloric acid and cautiously neutralising the extract with ammonia. This substance melts above 360°, and its molecular formula is $(C_9NH_5S)_2$; it is thus isomeric with the substance obtained in a similar manner from quinoline (Abstr., 1897, i, 103), and the methyl group must therefore have become replaced by hydrogen. The yield of this new substance is small; it is oxidised by dilute nitric acid to nicotinic acid; it is not reduced by zinc dust and acetic acid; when it is sublimed under diminished pressure, only traces of hydrogen sulphide are formed, and no sulphur is removed when the vapour of the substance is passed over heated copper turnings; it has feebly basic properties.

When the chloride SCl_2 is employed instead of S_2Cl_2, some of the same sulphur compound is obtained, together with 1 : 3-dichloroquinoline and a *tetrachloroquinoline* melting at 121°; and in one experiment a small quantity of a monochloroquinoline melting between 30° and 40° was isolated. The methyl has been largely replaced by chlorine in this case.

Neither 3-hydroxyquinoline, 1-hydroxyquinoline, isoquinoline nor pyridine yields a sulphur compound when treated with sulphur chloride; from the first three substances respectively there were obtained instead a mono-, a di-, and a tri-chloro-derivative, melting at 187°, 179°, and 124°. C. F. B.

Quinaldine-3′-carboxylic Acid. By ADOLPH CLAUS and ERNST MOMBERGER (*J. pr. Chem.*, 1897, **56**, 373—389).—Ethylic 2′-methylquinoline-3′-carboxylate (quinaldine-3′-carboxylate), when nitrated at the ordinary temperature with a mixture of equal parts of nitric and sulphuric acids, yields a 1- and a 4-nitro-derivative, to the extent respectively of 45 and 40 per cent. of the theoretically possible amount; when the product is poured into water, the 4-nitro-compound remains in solution as the sulphate, whilst the 1-isomeride, being a weaker base, is precipitated. Neither ethylic salt forms a methiodide. Both are hydrolysed to the corresponding nitro-acids by heating with strong hydrochloric acid in an open vessel on the water bath, and from these acids, by heating them with 10 per cent. sulphuric acid at 150°, carbonic anhydride can be eliminated; the products are respectively yellow 1-*nitro-2′-methylquinoline*, which melts at 137° and is not volatile with steam, and colourless 4-*nitro-2′-methylquinoline*, which melts at 82° and does come over with steam (Buhl, *Diss. Freiburg i. B.*, 1897). Both ethylic salts, moreover, can be reduced by iron paste, with a drop of acetic acid, to the corresponding amido-compounds, and

these are hydrolysed by hydrochloric acid to the amido-acids, which can also be prepared by the reduction of the nitro-acids.

1-*Nitro-2'-methylquinoline-3'-carboxylic acid* is yellowish and melts and decomposes at 196°; the yellow *hydrochloride* decomposes at 204°; the *ethylic* salt is yellowish, melts at 137°, and forms an orange-yellow *platinochloride* (with $2H_2O$) which decomposes at 195°. 1-*Amido-2'-methylquinoline-3-carboxylic acid* is straw yellow, and melts and decomposes at 230°; its *silver* salt was prepared and analysed; the *ethylic* salt is almost colourless, melts at 99°, forms an orange *platinochloride*, with $2H_2O$, decomposing at 190°, and an orange *methiodide* decomposing at 170°, and can be converted by the Sandmeyer reaction into *ethylic 1-chloro-2'-methylquinoline-3'-carboxylate*, which melts at 92°, forms a yellow *platinochloride*, with $4H_2O$, decomposing at 205°, but no methiodide, and is hydrolysed by strong hydrochloric acid to 1-*chloro-2'-methylquinoline-3'-carboxylic acid*, which is yellow and melts at 216°.

4-*Nitro-2'-methylquinoline-3'-carboxylic acid* is yellow and melts at 236°; the yellowish-red *hydrochloride* melts and decomposes at 215°; the *ethylic* salt is yellowish, melts at 126°, and forms a reddish-yellow *platinochloride*, with $2H_2O$, which decomposes at 232°. 4-*Amido-2'-methylquinoline-3'-carboxylic acid* is orange-yellow, and melts and decomposes at 275°; the *ethylic* salt is almost colourless, melts at 110°, and forms a reddish-orange *platinochloride*, with $2H_2O$, decomposing at 224°, and a red *methiodide* which melts and decomposes at 198—200°.

2'-Methylquinoline-3'-carboxylamide (*quinaldine-3'-carboxylamide*) separates gradually when the corresponding ethylic salt is allowed to remain for weeks with a large excess of the strongest ammonia in a well-stoppered bottle at the ordinary temperature, or, better, at 40—50°. The greater part of the ethylic salt, however, is converted into the ammonium salt. C. F. B.

Condensation of Isatic Acid to form Derivatives of Cinchonic Acid. By Wilh. Pfitzinger (*J. pr. Chem.*, 1897, [ii], **56**, 283—320. Compare Abstr., 1886, 370; 1889, 412).—Isatic acid undergoes a series of reactions similar to those discovered by Friedländer in the case of orthamidobenzaldehyde (Abstr., 1892, 1106). With ketones and ketonic acids, it yields derivatives of cinchonic acid,

$$C_6H_4{<}^{CO\cdot COOH}_{NH_2} + \begin{matrix} CH_2R^{I} \\ | \\ CR^{II}O \end{matrix} = 2H_2O + C_6H_4{<}^{C(COOH):CR^{I}}_{N \;=\!=\!=\; CR^{II}} .$$

With acetaldehyde, it would not condense; it does react, however, with acetone, methyl ethyl ketone, acetophenone, deoxybenzoin, pyruvic acid, and ethylic acetoacetate. When the two radicles CH_2R^{I} and R^{II} are of unequal size, it is the larger that reacts with the CO group of the isatic acid. The method commonly adopted was to heat the ketone with the isatic acid, dissolved in excess of aqueous-alcoholic potash of about 12 per cent. strength, for several hours on the water bath in a reflux apparatus; in the case of deoxybenzoin, which is easily acted on by alkalis, it was found advisable to add it gradually to the already boiling alkaline solution of isatic acid; pyruvic acid and ethylic acetoacetate reacted at the ordinary temperature with excess of 33 per cent. aqueous potash, no alcohol being used.

Acetone yields 2′-methylcinchonic acid, $C_9NH_5Me\cdot COOH$ (Böttinger, Abstr., 1884, 320); this has both acid and basic properties. The yellow *platinochloride* melts and decomposes at 220°, and crystallises with $2H_2O$; the hydrobromide crystallises from water with $2H_2O$, from moderately strong hydrobromic acid with H_2O; the orange-red *dichromate* and the greenish-yellow *picrate*, the latter melting at 190—191°, are anhydrous; the *silver* salt was prepared and analysed, and many other salts are described. The *ethylic* salt, which was obtained by digesting the acid at the ordinary temperature with saturated absolute alcoholic hydrogen chloride, melts at 77°; its yellow *picrate* melts at 155—156°, and its yellow *platinochloride* melts and decomposes at 203° and crystallises with $2H_2O$. By heating the ethylic salt for several hours with a large excess of aqueous ammonia of sp. gr. = 0·880, it is converted into the *amide*, which melts at 239°, and forms a *picrate* melting and decomposing at 231—232°. 2′-Methylcinchonic acid, when it is heated with phthalic anhydride and zinc chloride at 170—180°, forms a *phthalone*, $COOH\cdot C_9NH_5\cdot CH:C<\genfrac{}{}{0pt}{}{C_6H_4}{O}>CO$, which melts and decomposes at some temperature above 300°.

Acetophenone yields 2′-phenylcinchonic acid, $C_9NH_5Ph\cdot COOH$ (Döbner, Abstr., 1887, 504); of this, the acid properties are well marked, but not so the basic, for the salts with acids are decomposed by water. The orange-yellow, anhydrous *platinochloride*, and the yellow *picrate* (not the normal compound, but $2C_9NH_5Ph\cdot COOH,C_6H_3N_3O_7$) were prepared and analysed; so also were the *calcium* and *silver* salts, with $2\frac{1}{2}$ and $\frac{1}{2}H_2O$ respectively, and the *ethylic* salt, which melts at 50—51°, and forms a greenish-yellow *picrate* melting at 144—145°, and a pale flesh-coloured *platinochloride* melting and decomposing at 210—211°. The acid itself is converted into 2′-methylquinoline by distillation with slaked lime.

Deoxybenzoin yields 2′ : 3′-*diphenylcinchonic acid*, $C_9NH_4Ph_2\cdot COOH$, which melts and decomposes at 295°, and has very feeble basic, but marked acid, properties. The yellowish-green *picrate* melts at 236°; the *sodium* and *calcium* salts, with $8H_2O$ and $9H_2O$ respectively, and the *silver* salt were prepared and analysed, but no ethylic salt could be obtained. The acid, when heated a little above its melting point, yields a substance that melts at 90—91° and boils at about 310° under 80 mm. pressure. This is probably 2′ : 3′-diphenylquinoline (Buddeberg, Abstr., 1890, 1142); its greenish-yellow *picrate* melts at 223—224°, and it forms a yellow *methiodide*, which has the character of a quaternary iodide, and decomposes at 231° into methylic iodide and 2′ : 3′-diphenylquinoline; the orange-red *platinochloride* of the corresponding *methochloride* was prepared and analysed.

Pyruvic acid yields 2′:4′-quinolinedicarboxylic acid, $C_9NH_5(COOH)_2$, (Döbner and Peters, Abstr., 1890, 176); this has no basic properties. The normal *potassium* salt, with $2\frac{1}{2}H_2O$, was prepared and analysed. When the acid is heated at 240°, it yields 4′-quinolinecarboxylic (cinchonic) acid, although, when it is distilled, quinoline is formed.

Methyl ethyl ketone yields 2 : 3-*dimethylcinchonic acid*,

$$C_9NH_4Me_2\cdot COOH,$$

which melts and decomposes above 310°; when distilled with slaked lime, it yields 2′ : 3′-dimethylquinoline (Rohde, Abstr., 1889, 523).

Ethylic acetoacetate yields *2′-methylquinoline-3′ : 4′-dicarboxylic acid*, $C_9NH_4Me(COOH)_2 + H_2O$, which melts and decomposes at 236—237° when heated slowly; its *silver* salt was prepared and analysed.

Paramethylisatic acid reacts with acetone in the same manner as isatic acid; the product is *3 : 2′-dimethylcinchonic acid*,

$$C_9NH_4Me_2\cdot COOH;$$

this melts and decomposes at 261°, and has both basic and acid properties; the flesh-coloured *platinochloride*, which melts and decomposes at 243—244° and crystallises with $2H_2O$, and the *silver* salt were prepared and analysed. When the acid is distilled with lime, it yields 3 : 2′-dimethylquinoline (Döbner and Miller, Jacobsen and Reimer, Abstr., 1884, 184, 335). C. F. B.

Existence of Condensation Rings with Para-Linking. II. By Albert Ladenburg and W. Herz (*Ber.*, 1897, **30**, 3043—3045. Compare Abstr., 1897, i, 485).—Rosdalsky, by observing the depression of the freezing point of phenol brought about by the substance described by him as 1 : 4-methylenepiperazine, $C_4N_2H_8{:}CH_2$ (Abstr., 1896, i, 257), found the molecular weight of that substance to be 80—84 (calculated 98). The authors have obtained numbers varying irregularly between 52 and 79·5, from which they conclude that the substance is decomposed in phenol solution, and, as a matter of fact, it cannot be recovered from that solution. They regard it as a polymeride, in which case the assumption of a para-linking is no longer necessary. C. F. B.

Tartrazines. By Robert Gnehm and Louis Benda (*Annalen*, 1897, **299**, 100—130. Compare Abstr., 1896, i, 678; also Anschütz, Abstr., 1897, i, 258).—In view of the constitutional formula for tartrazine put forward by Anschütz (*loc. cit.*), the authors have modified their formula for the colouring matter obtained by the action of paranitrodiazobenzene chloride on an alkaline solution of tartrazine, regarding it as having the constitution $\begin{matrix} N\!=\!=\!=\!=\!C(COONa) \\ | \\ N(C_6H_4\cdot SO_3Na)\cdot CO \end{matrix}\!\!>\!C{:}N\cdot NH\cdot C_6H_4\cdot NO_2$.

The *barium* salt is an amorphous, orange-yellow powder, and dissolves in water with difficulty; the *silver* salt crystallises in cinnabar-red prisms, and forms a yellow solution in water.

The colouring matter itself is obtained also from paranitrophenylhydrazine, dihydroxytartaric acid, and paraphenylhydrazinesulphonic acid; the yield, however, is small, owing to the fact that paranitrophenylhydrazine converts dihydroxytartaric acid into the osazone instead of the hydrazone.

Paranitrophenylhydrazinedihydroxytartaric *osazone* is prepared by the action of the hydrazine on dihydroxytartaric acid at common temperatures; it is a yellow substance which becomes red on exposure to air. It is somewhat soluble in hot water, forming a yellow solution, and it dissolves also in alcohol, becoming in part converted into the pyrazolone derivative; caustic alkalis give rise to a beautiful blue solution, which becomes dirty brown when diluted with much water.

Alcoholic ferric chloride develops a reddish-brown coloration which is taken up by ether. The osazone is capable of losing water in two ways, producing (1) a pyrazolone derivative, or lactazam, owing to elimination of water from one imido-group and the more remote carboxylic radicle and (2) an acid anhydride, by elimination of water from the two carboxylic groups. The first of these changes is brought about by heating the osazone with aqueous hydrochloric acid, glacial acetic acid, 95 per cent. alcohol, or a dilute solution of sodium carbonate; conversion into the anhydride, on the other hand, results from heating the osazone alone, or with acetic anhydride or benzoic chloride.

1-*Paranitrophenyl*-3-*carboxyl*-4-*paranitrophenylhydrazonepyrazolone* is the product of the former change; after crystallisation from acetic anhydride, it melts and decomposes at 238—240° (uncorr.). The solution in caustic soda is brown, and in concentrated sulphuric acid orange red. The *sodium* salt crystallises in orange needles or scales containing $1H_2O$, and the *barium* salt is anhydrous; the *silver* salt is brown, and the *mecurous* and *lead* salts orange.

The *anhydride*, $C_{16}H_{10}N_6O_7$, of the osazone, obtained by the second series of agents, crystallises from acetic anhydride in red prisms, and melts at 278—280°, when it becomes black and evolves gas. It is insoluble in boiling water, but slowly forms a reddish-brown solution in boiling sodium carbonate, which regenerates the osazone; the solution in caustic soda is blue, owing to the immediate production of the osazone.

The authors have repeated the experiments of Ziegler and Locher (Abstr., 1887, 578) who state that acetic anhydride converts diphenylizindihydroxytartaric acid into an acetyl-anhydride which melts at 234°; they find that this compound is not really an acetyl derivative, but an anhydride arising from the dehydrating action of acetic anhydride and of benzoic chloride. When this substance is boiled with a five per cent. solution of caustic soda, 1-phenyl-3-carboxyl-4-phenylhydrazonepyrazolone is produced.

Ziegler and Locher state that monophenylizindihydroxytartaric acid, the hydrazone of dihydroxytartaric acid, is produced from phenylhydrazine and the acid, even in presence of excess of the latter, when the action proceeds at common temperatures; this does not apply in the case of paranitrophenylhydrazine, which in the cold, and in the presence of excess of dihydroxytartaric acid, yields the osazone. The authors find that a mixture of osazone with hydrazone is produced in the case of phenylhydrazine, whilst metanitrophenylhydrazine yields principally osazone with a small proportion of hydrazone. M. O. F.

New Methods for the Preparation of Anhydro-compounds. By Stefan von Niementowski (*Ber.*, 1897, 30, 3062—3071).—It has been previously shown (Abstr., 1895, i, 571) that the amides of fatty acids readily react with orthamidobenzoic acid, yielding δ-hydroxyquinazoline derivatives. The condensation of acid amides and of ethereal salts with orthamidophenols and with orthodiamine hydrochlorides has now been investigated (compare Kelbe, Abstr., 1883, 915; R. Meyer and Seeliger, Abstr., 1896, i, 45). When equivalent quantities of formamide and of orthamidophenol are subjected to dry distillation, Ladenburg's benzoxazole melting at 30° is produced.

A theoretical yield of O. Fischer's 3-methylbenzimidazole is obtained by heating together formamide and metaparatolylenediamine hydrochloride $[CH_3 : (NH_2)_2 = 1 : 3 : 4]$; it melts at 114°. Acetamide and the same salt, when heated to 180°, give Hobrecker's ethenyltolylenediamine melting at 200—202°.

β-Phenylmetatolimidazole is obtained from benzamide and metaparatolylenediamine hydrochloride.

β-Orthamidophenylbenzimidazole, $C_6H_4<\begin{smallmatrix}NH\\N\end{smallmatrix}>C\cdot C_6H_4\cdot NH_2$, is formed when equivalent quantities of orthamidobenzamide and of orthophenylenediamine hydrochloride are heated at 190° for 3 hours; it is purified by rubbing in a mortar with strong alkali, and subsequent solution in hot alcohol, and can be freed from a dye which accompanies it by the addition of boiling water to the alcoholic solution and quick filtration, when the whole of the colouring matter will be found on the filter. The pure imidazole crystallises in colourless, flat, monoclinic prisms melting at 211°. It is readily soluble in boiling alcohol or chloroform, moderately in benzene or ether, and very sparingly in hot water. It dissolves readily in acids, but not in alkalis. Its *hydrochloride*, $C_{13}H_{11}N_3,2HCl$, is only sparingly soluble in boiling alcohol or water and melts at 275°. The *platinochloride*, $C_{13}H_{11}N_3,H_2PtCl_6$, crystallises in yellow needles, blackens at 250—280°, and is readily decomposed in solution yielding metallic platinum.

β-orthamidophenylpara- (? meta) -tolimidazole is formed by the action of orthamidobenzamide on metaparatolylenediamine hydrochloride; it crystallises in pearly, glistening, six-sided plates melting at 189°. *β-Orthamidoparatolylbenzimidazole*, from orthophenylenediamine hydrochloride and orthamidotolylamide, crystallises from alcohol in glistening plates and from toluene in needles, melts at 203°, is readily soluble in cold acetone or acetic acid, in boiling alcohol or toluene, is but moderately soluble in ether, and practically insoluble in water. The *nitrate* is readily soluble, but the *hydrochloride*, $C_{14}H_{13}N_3,HCl$, and *sulphate* only sparingly. The product from orthamidotolylamide and metaparatolylenediamine hydrochloride crystallises in little rods melting at 188°. When orthamidophenol (20 grams) is boiled with ethylic acetoacetate for 18 hours and the product subjected to fractional distillation, the chief products are orthacetamidophenol and β-methylbenzoxazole; metatolimidazole and ethylic chloride are the products formed when equivalent quantities of ethylic formate and metaparatolylenediamine are heated in sealed tubes for 3 hours at 225°. Similar experiments with ethylic acetate gave but a small quantity of ethenyldiamidotoluene. J. J. S.

A Method of Preparing Phthalazines. By Siegmund Gabriel and Georg Eschenbach (*Ber.*, 1897, 30, 3022—3037).—By acting with hydrazine on ketonic orthocarboxylic aids, $CRO\cdot C_6H_4\cdot COOH$, and treating the phthalazone, $C_6H_4<\begin{smallmatrix}CR\\CO\end{smallmatrix}>N_2H$, which is formed with phosphorus oxychloride, a chlorophthalazine, $C_6H_4<\begin{smallmatrix}CR\\CCl\end{smallmatrix}>N_2$, is obtained. When this is heated with hydriodic acid and phosphorus at

200°, a simple reduction to the phthalazine, $C_6H_4<\substack{CR \\ CH}>N_2$, does not take place; one of the nitrogen atoms is eliminated as ammonia, and a dihydroisoindole, $C_6H_4<\substack{CHR \\ CH_2}>NH$, is formed, occasionally also an isoindole. It is now found that the desired reduction to a phthalazine can be effected, in the case of 4-chlorophthalazine and 1 : 4′-chloromethylphthalazine, by boiling these substances with hydriodic acid (boiling at 127°) and red phosphorus.

1′ : 4′-Methylchlorophthalazine (Abstr., 1893, i, 348) is obtained by heating 1′-methylphthalazone (50 grams) for ½ hour on the water bath with phosphorus oxychloride (100 c.c.) and pouring the product into ice and water. The orange-red *platinochloride*, $2C_9H_7ClN_2,H_2PtCl_6$, is still unmelted at 280°; the yellow *aurochloride*, $2C_9H_7ClN_2,HAuCl_4$, and *picrate*, $C_9H_7ClN_2,C_6H_3N_3O_7$, melt at 149—150° and 154° respectively; the red *ferrocyanide*, $2C_9H_7ClN_2,H_4Cfy$, crystallises in hexagonal plates. When methylchlorophthalazine is boiled for 1 hour with hydriodic acid and phosphorus, the product is 1′ : 4′-methyliodophthalazine, melting at 116°, the orange-yellow *platinochloride* of which, $2C_9H_7IN_2,H_2PtCl_6$, remains unmelted at 280°. When the boiling is continued for 9 hours or more, until there is no solid remaining in the flask except the phosphorus, 1′-*methylphthalazine*, $C_6H_4<\substack{CMe:N \\ CH=N}$, is formed; this is deliquescent, melts at 74·5°, and boils at 204°, 210—213°, and 322—324° (with partial decomposition) under pressures of 25 mm., 40 mm., and 1 atmo. respectively; some 1′-methylphthalazone and methylisoindole are also formed in the reaction. 1′-Methylphthalazine behaves generally as a monacid base; the *hydrochloride* melts and decomposes at 222—223°, the yellowish *hydriodide* at 287°, and the lemon-yellow *aurochloride* and *picrate* at 175° and 205° respectively; the *nitrate* decomposes at 159°, the orange-red *dichromate* at 170°; the reddish-orange *ferrocyanide*, $2C_9H_8N_2,H_4Cfy$, is unmelted at 290°. Reduction with zinc and hydrochloric acid converts the base into methylisoindole, not to a base $NH_2·CH_2·C_6H_4·CHMe·NH_2$, as the analogy with phthalazine (Abstr., 1893, i, 732) would lead one to expect. Sodium amalgam does, however, reduce it to 1′-*methyltetrahydrophthalazine*, $C_6H_4<\substack{CHMe \\ CH_2}>N_2H_2$, a monacid base the *hydrochloride* and *picrate* of which melt and decompose at 190° and 146° respectively, whilst the *dibenzoyl* derivative melts at 185°. With methylic iodide in cold methyl-alcoholic solution, 1′-methylphthalazine forms a *methiodide* which melts and decomposes at 142—143°; when this is distilled with aqueous potash, the distillate contains 1′ : 3′-*dimethyldihydrophthalazine*, $C_6H_4<\substack{CMe:N \\ CH_2·NMe}$, a monacid base the *hydrochloride* of which melts at 245°, and the lemon-yellow *picrate* and orange-yellow *platinochloride* decompose at 120° and 230° respectively, whilst the residue in the flask contains 1′ : 3′-*dimethylphthalazone*, $C_6H_4<\substack{CMe:N \\ CO·NMe}$, which melts at 109—110°, and can also be prepared

by methylating 1′-methylphthalazone. 1′-Methylphthalazine exhibits some of the condensation reactions of 2′-methylquinoline (quinaldine): heated for three-quarters of an hour at 200—210° with phthalic anhydride in an atmosphere of carbonic anhydride, it yields a yellow phthalone, $\begin{matrix} C_6H_4-C\cdot CH:C_8H_4O_2 \\ CH:N\cdot N \end{matrix}$, melting at 260°; with excess of chloral at 55—60°, it yields 1′-*trichlorohydroxypropylphthalazine*, $C_8N_2H_5\cdot CH_2\cdot CH(OH)\cdot CCl_3$, which melts and decomposes at 180°, and is hydrolysed by methyl-alcoholic potash to *phthalazine*-1′-*acrylic acid*, $C_8N_2H_5\cdot CH:CH\cdot COOH$, which melts and decomposes at 200°, and is also a monacid base, the *hydrochloride* and yellow *aurochloride* decomposing at 218° and 166° respectively, whilst the *picrate* melts and decomposes at 157—158°, and the orange-red *platinochloride* is unmelted at 270°. With benzaldehyde at 100°, 1′-methylphthalazine yields the yellow 1′-*cinnamenylphthalazine*, $C_8N_2H_5\cdot CH:CHPh$, melting at 115°, which can be reduced by boiling with hydriodic acid and phosphorus to 1′-*phenylethylphthalazine*, $C_8N_2H_5\cdot CH_2\cdot CH_2Ph$, melting at 112·5—113·5°, a monacid base of which the yellowish *hydriodide* melts at 212—220°, and the *nitrate* decomposes at 135—136°.

Incidentally, it is mentioned that the *anhydride* of diphthalaldehydehydrazonic acid (Liebermann and Bistrzycki, Abstr., 1893, i, 372) melting at 219—220°, is obtained when phthalazone is prepared from phthaldehydic acid by the action of hydrazine; and that, when 1′-methylphthalazone is methylated, the *hydrazone-methiodide* of *acetophenonecarboxylic acid*, $COOH\cdot C_6H_4\cdot CMe:N_2H_2,MeI$, melting and decomposing at 201°, is formed. C. F. B.

Syntheses in the Phenanthridine Group. By AMÉ PICTET and A. GONSET (*Chem. Centr.*, 1897, i, 413; from *Arch. Sci. phys. Genève*, [iv], 3, 37—51).—*Orthophenylbenzaldehyde*, $C_6H_4Ph\cdot COH$, formed when a mixture of calcium formate and calcium orthophenylbenzoate is distilled, is a bright yellow oil which boils at 310° without decomposition, and yields a *phenylhydrazone* melting at 115°; its *oxime* melts at 112·5°, and, on being heated with zinc chloride at 280—300°, loses $1H_2O$, yielding phenanthridine.

When fluorenone oxime is heated with zinc chloride, the Beckmann transformation takes place, and a yield of 30 per cent. of phenanthridone is obtained.

Orthonitrobenzanilide, $NO_2\cdot C_6H_4\cdot CO\cdot NHPh$, prepared from orthonitrobenzoic chloride and aniline, crystallises from alcohol or benzene in white needles, and melts at 155°. On reduction with ammonium sulphide, it yields *orthamidobenzanilide*, which crystallises from benzene in lustrous needles, and melts at 131°. On diazotising a sulphuric acid solution of this substance, and boiling, *phenyl-β-phenotriazone*, $C_6H_4 \begin{matrix} \diagup CO\cdot NPh \\ \diagdown N{=\!=}N \end{matrix}$, is obtained, instead of phenanthridone; this crystallises from dilute alcohol in slender needles, melts at 150—151°, is almost insoluble in water, ether, and light petroleum, more soluble in alcohol and benzene, and very soluble in chloroform; its formation is explained by assuming a separation of sulphuric acid to take place

from the benzanilide-diazosulphate, according to the following equation.

$$C_6H_4<\begin{matrix}CO\cdot NHPh\\N{:}N\cdot SO_4H\end{matrix} = C_6H_4<\begin{matrix}CO\cdot NPh\\N{=}N\end{matrix} + H_2SO_4.$$

In order to avoid such a separation, it is necessary to employ an anilide in which an alkyl radicle is substituted for the hydrogen of the imido-group. *Orthonitrobenzoylmethylanilide*, prepared from methylaniline and orthonitrobenzoic chloride, crystallises in white needles, and melts at 94·5°. *Orthamidobenzoylmethylanilide* crystallises from benzene in prisms and melts at 127°. When diazotised in hydrochloric acid solution, and heated, nitrogen is evolved, and *n*-methylphenanthridone (Pictet and Patri, Abstr., 1893, i, 722), is obtained.

When benzanilide is distilled through a red-hot tube packed with pumice, a molecule of hydrogen is eliminated and phenanthridone is formed; benzylaniline, when similarly treated, yields a mixture of phenanthridine and acridine, together with a primary base, which is probably paramidodiphenylmethane, formed by the molecular transformation of benzylaniline. The formation of acridine is explained by assuming that ortho- as well as paramidodiphenylmethane results from this transformation, and that this, by the loss of $2H_2$, is transformed into acridine (compare Abstr., 1894, i, 200).

W. A. D.

Action of Chloroform and Alcoholic Potash on Phenylhydrazine. By SIEGFRIED RUHEMANN (*Ber.*, 1897, **30**, 2869—2871. Compare Ruhemann and Elliott, Trans., 1888, **53**, 850).—The compound produced by the action of chloroform and alcoholic potash on phenylhydrazine (*loc. cit.*) is also obtained by heating formophenylhydrazide (Abstr., 1897, i, 468), and has been called diphenyltetrazoline by Pellizzari (Abstr., 1897, i, 231).

Amidodiphenyltetrazoline, $C_{14}H_{11}N_4\cdot NH_2$, obtained by reducing nitrodiphenyltetrazoline with stannous chloride and hydrochloric acid, crystallises from dilute alcohol in needles, and melts at 188°. The *hydrochloride* forms colourless needles. M. O. F.

The Alleged Synthesis of Xanthine from Hydrogen Cyanide. By EMIL FISCHER (*Ber.*, 1897, **30**, 3131—3133).—The author has repeated Gautier's experiments (Abstr., 1885, 275), who, by heating hydrogen cyanide with acetic acid at 145°, obtained a substance which gave the reactions of xanthine. Only 0·16 gram was obtained by the author from 40 c.c. of dry hydrogen cyanide, and this gave the reactions described by Gautier, but did not yield murexide when the residue obtained by evaporating with chlorine water was moistened with ammonia. Since a mixture of the compound with one-tenth of its weight of xanthine gave this murexide reaction distinctly, it follows that the substance obtained from hydrogen cyanide was not xanthine.

A. H.

The Alkylates of Papaverine. By ADOLPH CLAUS and OSKAR KASSNER (*J. pr. Chem.*, 1897, [ii], **56**, 321—345. Compare Abstr., 1893, i, 489).—When papaverine propobromide, $C_{20}H_{21}NO_4,CH_2EtBr$, is decomposed by aqueous alkalis, yellow masses separate if the

alkali is not too dilute; these dissolve in ether, and on evaporating the solution a yellow oil is obtained. This is *propylidenepapaverinium*, $C_{20}H_{21}O_4$⫶N⁚CHEt; it is insoluble in water, but in contact with it, or even when dissolved in moist ether, it is slowly converted into *propylpapaverinium hydroxide*, $C_{20}H_{21}O_4$⫶N(OH)·CH_2Et. This dissolves in water, imparting to it an alkaline reaction, and it is also soluble in moist ether; by the addition of plenty of dry ether to the latter solution, it can be obtained in unstable, colourless crystals. The presence of but a trace of alkali is sufficient to transform it into the yellow propylidenepapaverinium. In the presence of alcohol, it loses its alkaline reaction, becoming converted into *propylpapaverinium ethoxide*, $C_{20}H_{21}O_4$⫶N(OEt)·CH_2Et; this is also formed when the yellow base is dissolved in alcohol, or when an alcoholic solution of papaverine proposulphate or propochromate is decomposed with lead hydroxide, and it can be obtained in colourless crystals, which melt at 137°, by adding ether to the alcoholic solution; its character is rather that of a salt. All the three substances described are converted by hydrogen chloride or hydrochloric acid into yellow *papaverine propochloride*, $C_{20}H_{21}O_4$⫶NCl·CH_2Et, which melts at 80°.

Papaverine ethobromide and methiodide appear to yield each a similar series of compounds, but the reactions are less easy to study than in the case of the propyl derivatives. The benzochloride is even more readily converted by alkalis into *benzylidenepapaverinium*, $C_{10}H_{21}O_4$⫶N⁚CHPh, and this was obtained in yellow needles melting at about 130°; when its ethereal alcoholic solution is allowed to evaporate spontaneously in the air, oxidation takes place and colourless crystals are obtained of a neutral substance which melts at 165° and appears to have the molecular formula, $C_{14}H_{15}NO_3$.

In the course of attempts to obtain papaverinium hydroxides, a few dichromates, [$C_{20}H_{21}O_4$⫶N(CH_2R)]$_2Cr_2O_7$, and sulphates, [$C_{20}H_{21}O_4$⫶N(CH_2R)]$_2SO_4$, were prepared; these were the yellow *benzochromate*, reddish-brown *ethochromate* melting at 139°, hygroscopic *methosulphate* melting at about 110°, and *proposulphate* which melts at 126° and crystallises with $2H_2O$.

Just as papaverine is converted into papaveroline by heating with hydriodic acid, four methoxy-groups being exchanged for hydroxyl, so the alko-haloids of papaverine, $C_{20}H_{21}O_4$⫶NX·CH_2R [R = H,Me,Et,Ph; X = Cl,Br,I], yield the corresponding derivatives of papaveroline, $C_{16}H_{13}O_4$⫶NX·CH_2R, the alko-chlorides when heated with hydrochloric acid at 160—180°, the alko-bromides with hydrobromic acid at 130—140°, and the hydriodides with hydriodic acid (and a little amorphous phosphorus) at 130°. In this way, the following derivatives of *papaveroline* were prepared (the numbers given are melting points). *Benzochloride*, 158°; *methochloride*, 235°; *ethochloride*, 215°, these are greenish; *propobromide*, 140°, yellowish; methiodide, 77°, reddish-brown.

C. F. B.

A New Alkaloid from Retama Sphærocarpa. By J. A. Battandier and Th. Malosse (*Compt. rend.*, 1897, 125, 360—362; see also this vol., i, 52).—The authors have extracted from the young shoots and bark of *Retama sphærocarpa* a new alkaloid, *retamine*,

which they regard as a hydroxysparteine, $C_{15}H_{26}N_2O$; it differs, however, from all the known artificial hydroxysparteines. It crystallises from light petroleum in long needles melting and decomposing at 162°. It is sparingly soluble in water or ether, but dissolves readily in alcohol or light petroleum; when obtained by spontaneous evaporation from its alcoholic solution, it forms large, rectangular plates. The alkaloid colours phenolphthalein, and is a strong base, forming a series of well-defined salts; these salts contain either one or two molecules of a monobasic acid to one molecule of the alkaloid. The salts are decomposed by caustic potash or by large quantities of ammonia, but the base itself is sufficiently strong to decompose ammonium salts, and it also precipitates ferric and cupric hydroxides from solutions of these metals. It has strong reducing properties, is dextrogyrate, yields no precipitate with platinic chloride, and gives a feeble sparteine reaction with ammonium sulphide. J. J. S.

New Bile Pigments. By A. Dastre and N. Floresco (*Compt. rend.*, 1897, **125**, 581—583).—In addition to bilirubin, which the authors call the original pigment, and biliverdin, which they call the definite or final pigment, the biles of many animals contain two others which they call *biliprasinic* or *intermediate pigments.* Biliprasinic-yellow exists in the bile of the calf and in other yellow biles; it is changed to green (biliprasinic-green) by the action of carbonic anhydride, glacial acetic acid, and other acids, especially in presence of alcohol, is unstable in a vacuum, and is decomposed by light. Biliprasinic-green exists in the fresh bile of the ox, the rabbit, and other animals. Alkalis convert it into biliprasinic-yellow, this being the alkaline pigment, whilst the green is the acid pigment. In a vacuum, it changes into bilirubin. The characteristic difference between the biliprasinic pigments on the one hand, and bilirubin and biliverdin on the other, is that the biliprasinic acid is displaced from its combination with alkalis by carbonic anhydride, whilst bilirubin and biliverdin displace carbonic acid. All the pigments are derived from bilirubin by oxidation and hydration, and the biliprasinic acid is intermediate between it and biliverdin. The chief agents in bringing about these changes, except that of biliprasinic-yellow into biliprasinic-green or *vice versâ,* are oxygen, which is indispensable, heat, light, and alkalis and acids. Marked alkalinity increases the stability of bilirubin, neutrality or acidity accelerates the formation of biliprasinic-green. Heat tends to change bilirubin into biliprasinic-green, and the latter into biliverdin, but prolonged heating at 100° decomposes the bilirubinates. Light rapidly converts bilirubin into biliprasin, and the latter into biliverdin. It is probable that the oxidation and hydration of bilirubin begins in the hepatic cellules and the biliary canaliculi; in all cases, these changes continue in the gall-bladder. The artificial conditions of the transformation are not realised in the animal body, and it is necessary to assume the existence of a particular oxidising agent, or a particular condition in the organism, occurring in the liver, and passing in part into the bile. C. H. B.

Organic Chemistry.

The Relation of Electrochemistry to Organic Chemistry. By KARL ELBS (*Zeit. Elektrochem.*, 1897, **4**, 81—89).—An historical account is given of the researches of Kolbe, Kekulé, Crum Brown and Walker, von Miller and Mulliken and Weems on the electrolysis of salts of organic acids, and the connection between the conductivity of solutions of organic acids and their constitution and basicity is mentioned. Electrolytic reduction and oxidation processes are then considered, the researches of Goppelsroder, Gattermann, and Clement and Noyes being described. Of interest is the production of naphthazarine by the electrolytic reduction of 1 : 2′ or 1 : 4′-dinitronaphthalene dissolved in sulphuric acid. By the electrolytic oxidation of paranitrotoluene, paranitrobenzylic alcohol may be prepared, a result not attainable by any chemical oxidising agent. The electrolytic product, ammonium persulphate, possesses specialised oxidising properties which are not found in any other oxidising agent ; by its means orthonitrophenol and salicylic acid may be oxidised directly to nitroquinol and to quinolcarboxylic acid respectively, whilst anthraquinone is oxidised to alizarin, and alizarin to alizarin-bordeaux and alizarin-cyanine.

T. E.

[The Number of Isomeric Paraffins.] By F. HERRMANN (*Ber.*, 1898, **31**, 91).—A reply to Losanitsch (this vol., i, 165).

Decomposition of Hexane and Trimethylethylene by Heat. By FRITZ HABER and H. OECHELHÄUSER (*Chem. Centr.*, 1897, i, 86, 225—226 ; from *J. Gasbel.*, **39**, 799—805, 813—818, 830—834).—In continuation of the work of Haber and Samoylowicz (Abstr., 1897, i, 307—308), the authors have investigated the decomposition of these gases at 900—1000° by passing them through a porcelain tube encased in a tube of platinum, platinum-iridium, or carbon which was heated electrically, the temperatures being measured by means of Le Chatelier's couple.

At 900—1000°, hexane is decomposed, yielding 29·22 per cent. of tar, 27·77 of methane, 22·14 of olefines, 6·76 (to 10) of benzene, 3·27 of carbon, 2·44 of hydrogen, and 1·1 of acetylene ; the last four products probably result from bye-reactions. Only a small quantity of naphthalene was detected. The tar consists probably of a condensation product of the olefines, since it chars on nitration. In comparison with the decomposition at lower temperatures, more acetylene and benzene are formed, but the smaller quantity of olefines produced causes, on the whole, a diminution in the illuminating value of the gas. The authors now fix the limit to which hexane may be heated without producing much carbon and hydrogen at 940°.

The decomposition products obtained by heating trimethylethylene at 668—790° are similar to those obtained from hexane, and only a little carbon and hydrogen are formed. The tar, however, contains olefines with higher molecular weights than trimethylethylene ; this is due to the instability of the primary decomposition products, which

have higher molecular weights than those obtained from hexane, and combine to form more complex compounds. The absence of any higher paraffins in the tar is also remarkable. Trimethylethylene when heated at 933—938°, forms a light brown vapour, which has the odour of naphthalene, the products of decomposition being 27·72 per cent. of methane, 8·10 of ethylene, 1·76 of hydrogen, 4·46 of gaseous bye-products, 0·30 of acetylene, 5·09 of carbon, 8·00 to 13·41 of benzene, and 33·71 to 39·12 of tar. The quantity of benzene formed is greater than at lower temperatures, just as in the case of hexane, and, similarly, more methane is produced than corresponds with the removal of 1 mol. from 1 mol. of the original substance. The formation of benzene must depend on an initial production of acetylene, for hexane and trimethylethylene do not contain any long carbon chain in common. Trimethylethylene, when heated at 1050—1060°, is decomposed largely into carbon and naphthalene, hence at temperatures over 950° only complicated secondary actions take place.

Benzene, when heated at 900°, remains practically unchanged, but decomposes between 900° and 1000°, forming higher aromatic compounds, which are different, however, from those present in the tar obtained from hexane and trimethylethylene at these temperatures, and must result, therefore, from the combination of benzene with other compounds, especially acetylene. Diphenyl and a crystalline substance boiling at above 254° were found in the decomposition products of benzene, but neither naphthalene nor styrene was present, and only a small quantity of acetylene.

Acetylene when heated at 600—800° forms a tar very rich in benzene, but containing only small quantities of aliphatic compounds. No flash of light was produced by the decomposition, as Lewes observed, except when air was present in the gas. E. W. W.

Laboratory Apparatus for preparing Gas from Light Petroleum. By Pietro Bartòlotti (*Gazzetta*, 1897, **27**, ii, 335—347).—The author has devised an apparatus for preparing heating or illuminating gas from light petroleum; it consists of two gasometers, connected with a carburetting cylinder filled with wood-wool, kept saturated with light petroleum, which saturates air passing through the carburetter. The air saturated with petroleum is drawn off to be burnt; in order to prevent firing back, a plug of wire gauze is used. W. J. P.

Recent Developments in Gas Lighting. By Hans Bunte (*Ber.*, 1898, **31**, 5—25).—An address delivered before the German Chemical Society. In the manufacture of coal-gas, the chief advance consists in the substitution of gaseous fuel for direct-heating, and the introduction of sloping instead of horizontal retorts. In Germany, notably in Westphalia and Silesia, large quantities of coal are carbonised for the sake of the coke, tar, and ammonia; a large quantity of benzene is obtained from the gases of these coke-furnaces, and the price of benzene has been so lowered thereby that it is extensively used for carburetting, and increasing the luminosity of coal gas; in this way, it is possible to obviate the necessity of mixing expensive coals, such as cannel and boghead, with coal which otherwise would give a gas of poor illuminating power. In America, illuminating gas is made largely by mixing

the vapour of low-boiling petroleum, or the decomposition products of the high-boiling fractions, with water-gas; this process is also being adopted in countries where these petroleum residues are to be had cheap, as in England, Belgium, Holland, and Denmark.

F. Siemens increased the amount of luminosity obtainable from coal-gas by means of a regenerative burner, in which the air supplied to the burner underwent a preliminary heating; a greater improvement was effected by the incandescent burner of Auer von Welsbach, in which a mantle of metallic oxides is heated to incandescence by a mixture of coal gas and air, burning underneath with a non-luminous flame. The mantles are woven of cotton gauze, and are impregnated with a mixture of thorium and cerium nitrates, dried, and eventually ignited; they contain 98—99 per cent. of thorium oxide, and 1—2 per cent. of cerium oxide; these are the most favourable proportions for luminosity: mantles of pure thorium oxide or pure cerium oxide give hardly any light at all. Experiments made by the author have shown that this mixture has no specially great emissive power for light rays; it, and the pure oxides, as well as carbon and magnesia, appear almost equally luminous when heated to the same high temperature. The explanation is to be sought in the catalytic action of cerium oxide, which lowers the kindling temperature of a mixture of hydrogen and oxygen from 650° to 350°. The mixture of air with the partly burned coal-gas rising from the burner at the foot of the mantle (a bunsen burner only sucks in about half the air needed to burn the gas completely) impinges on the particles of cerium oxide, and is brought by the action of the latter into extremely vigorous combustion; the great heat generated in this combustion makes the particles incandescent. Thorium oxide has no such catalytic action, and in consequence its presence might be thought prejudicial. The use it serves is in separating the particles of cerium oxide, for it is very voluminous when prepared by heating the nitrate. Cerium oxide, on the other hand, is fairly compact when so prepared, and a mantle made of it alone is but feebly luminous; this is probably because the heat is conducted away too fast, and the temperature never rises to that necessary for incandescence. The objection that the quantity of cerium oxide in a mantle is too small to produce so great a light is met by an approximate calculation, in which it is shown that the weight of cerium oxide in an incandescent burner of 70 candle power is about 4 milligrams, whilst the weight of incandescent carbon, present at any moment, in a luminous gas-flame of 20 candle power is about 0·1 milligram.

Mention is also made of acetylene as a source of light; it has found no extensive use as yet, because it is liable to explode when kept under pressure, or when subjected to a comparatively slight rise of temperature, and because of its great range of explosibility when mixed with air, any mixture containing between 5 and 80 per cent. of acetylene being explosive. In other respects, acetylene has great advantages; the calcium carbide, from which it is prepared by the action of water, contains more light-giving power condensed in a given space than any other substance. A passing reference is made to the lighting of railway carriages by means of oil-gas (made from paraffin oil), alone or mixed with acetylene.

In spite of the introduction of electric lighting, the consumption of coal-gas in Germany has progressed at an increasing rate. With regard to efficiency and economy of lighting, the following table is interesting.

	Coal gas.					Acetylene.	Petroleum.	Spirit (Incandescent).	Electric (Incandescent).
	Ordinary burner.	Regenerative burner.	Incandescent.						
			Old form.	New form.	With compressed gas.				
Candle power per 10 cub. ft. per hour	38	64	142	170	283	437	94*	94*	...
20 candle power costs per hour	2·8*d.*	1·6*d.*	0·75*d.*	0·62*d.*	0·37*d.*	1·91*d.*	1·8*d.*	2·1*d.*	5·3*d.*

* Per kilo. per hour.

C. F. B.

Electrolytic Preparation of Iodoform. By KARL ELBS and A. HERZ (*Zeit. Elektrochem.*, 1897, **4**, 113—118. Compare Foerster and Meves, this vol., i, 166).—Solutions containing alcohol, sodium carbonate, and potassium iodide are placed in a porous cell containing an anode of platinum gauze; the cell stands in a solution of sodium carbonate, in which the nickel gauze cathode is immersed. The theoretical yield of iodoform should be 1·468 grams per ampère hour, but in practice some iodic acid and small quantities of organic iodine compounds other than iodoform are produced. The best yield of iodoform is obtained at from 60—70°; the amount of iodic acid formed also increases slightly with the temperature. An increase in the concentration of the sodium carbonate solution slightly diminishes the yield of iodoform and considerably increases the formation of iodate, whilst an increase in the concentration of the iodide or of the alcohol has the opposite effects. This is to be expected, because the greater the concentration of the carbonate the greater is the amount of oxygen liberated at the anode, whereas an increase in the amount of iodide will increase the relative quantity of iodine liberated, and a greater concentration of alcohol will provide a better opportunity for the iodine to react with it. With an anode solution containing 6 grams of sodium carbonate, 10 grams of potassium iodide, 20 c.c. of 96 per cent. alcohol, and 100 c.c. of water, the best results were obtained with a current density of 0·5 to 1 ampère per sq. dcm. of anode surface. The yield increases as the process is continued, provided the composition of the solution is maintained constant. A solution of the above composition, except that 5 instead of 6 grams of sodium carbonate were used, gave at 60°, with a current density at the anode not exceeding 1 ampère per sq. dcm., over 97 per cent. of the theoretical yield of iodoform. The diaphragm may be omitted if a small cathode, placed near the surface of the solution, is employed.

The iodoform produced is perfectly pure. When acetone is used in place of alcohol, very little iodoform is obtained, the product consisting mainly of iodoketones and condensation products of acetone. Attempts to prepare bromoform and chloroform in the way used for iodoform gave negative results. T. E.

Bromine Derivatives of 2:3-Dimethylbutane. By HENRY L. WHEELER (*Amer. Chem. J.*, 1898, 20, 148—153).—2 : 3-Dibromo-2 : 3-dimethylbutane, prepared from pinacone by the methods of Baeyer (Abstr., 1894, i, 45) and of Thiele (Abstr., 1894, i, 217), melts at 192°. When 1 molecular proportion of bromine is added to this in presence of iron wire, no tribromo-derivative is obtained, but 1 : 2 : 3 : 4-*tetrabromo*-2 : 3-*dimethylbutane*, $CH_2Br\cdot CMeBr\cdot CMeBr\cdot CH_2Br$, is immediately formed; this melts at 139°, and is also formed on adding bromine to the 2 : 3-dimethyl-1 : 3-butadiene obtained by the action of alcoholic potash on 2 : 3-dibromo-2 : 3-dimethylbutane.

When isobutylic bromide is heated with bromine in presence of iron wire, 1 : 2-dibromo-2-methylpropane is formed, although the yield is poor; Linnemann (Abstr., 1872, 478) states that he was unable by direct bromination to detect the formation of this compound.

W. A. D.

Regularities in the Boiling-points of Isomeric Aliphatic Compounds. By ALEXANDER NAUMANN (*Ber.*, 1898, 31, 30).—The author had long anticipated Menschutkin (this vol., i, 116) in noting these regularities (compare *Thermochemie*, p. 167; and this Journal, 1874, 529, 563). C. F. B.

Chemistry of Whiskey. By ALFRED H. ALLEN (*J. Fed. Inst. Brew.*, 1897, 3, 24—46).—An account is given of the manufacture of whiskey, and of the nature of its secondary constituents (higher alcohols, ethereal salts, &c.). The author finds that if spirit containing amylic alcohol is allowed to remain for some time in contact with oak or cork shavings, a large proportion of the amylic alcohol will be absorbed by the shavings, and he attributes the well-known effect of storing whiskey in oaken casks partly to this selective absorption. Analyses are given of the spirituous liquid obtained by steaming old whiskey casks; this is found to be very much richer in both fusel oil and ethers than whiskey itself. A. C. C.

Volatile Bye-products of Fermentation. By ALFRED C. CHAPMAN (*J. Fed. Inst. Brew.*, 1897, 3, 240—254).—An account is given of the better known volatile fermentation bye-products, and the manner in which they are formed is discussed. It is found that there is but little difference between the amounts of higher alcohols formed during the earlier and later stages of fermentation, and further that the quantities of these alcohols present in samples of beer which had been stored for more than twenty years were not sensibly greater than are usually found in recently made beers. These results are opposed to Lindet's supposition that these substances are not products of the normal fermentation of sugar, but that they are only formed under abnormal conditions of yeast life, consequent on the disappearance of the fermentable sugar. In an attempt to separate the ethereal salts

present in old beer, ethylic acetate and ethylic butyrate were identified. When fresh malt-wort is distilled, furfuraldehyde is always present in the distillate. An approximate estimation of the amount of this substance in the wort and also in the resulting beer showed that little, if any, had been formed during fermentation; it is therefore an unfermented wort constituent, and not a product of fermentation. Analyses are given showing the amounts of ethereal salts, higher alcohols, furfuraldehyde and acetaldehyde present in five samples of English beers; the effect of storage on the amounts of the above constituents was investigated, and analyses are given showing the quantities present in three samples of beer which had been in bottle from sixteen to twenty years.

Numbers are given showing the effects of high and low fermentation temperatures on the production of ethereal salts and higher alcohols; at the higher temperatures, increased quantities of both of these constituents are formed. Details are also given of the methods adopted for the estimation of the bye-products referred to in the paper.

A. C. C.

Action of Zinc on Monochloromethylic Ether. By MICHELE FILETI and AUSONIO DE GASPARI (*Gazzetta*, 1897, **27**, ii, 293—296).—No reaction occurs on boiling monochloromethylic ether with anhydrous zinc chloride, but on heating the ether with zinc, a violent reaction occurs, methylic chloride, zinc chloride, hydrogen chloride, methylal, and methylic-2-chlorethylic ether being produced.

Methylic 2-chlorethylic ether, $CH_2Cl\cdot CH_2\cdot OMe$, when isolated by fractional distillation, is a colourless liquid, heavier than water; it boils at 90—91° under 735·7 mm. pressure, and has the normal vapour density by V. Meyer's method at the temperature of boiling xylene. It does not fume in the air, thus contrasting with methylic 1-chlorethylic ether and chloromethylic ethylic ether (Favre, Abstr., 1895, i, 14); it is probably produced by a reaction represented by the equation, $CH_2Cl\cdot OMe + CH_3Cl = HCl + CH_2Cl\cdot CH_2\cdot OMe$, and is not affected by boiling with sodium, zinc, or zinc chloride, or by heating with sodium acetate or silver at 150°. W. J. P.

Chloromethylic Ethylic Ether. By AUSONIO DE GASPARI (*Gazzetta*, 1897, **27**, ii, 297—298).—The author has prepared chloromethylic ethylic ether, $CH_2Cl\cdot OEt$ (compare Favre, Abstr., 1895, i, 14), by saturating a mixture of aqueous formaldehyde and ethylic alcohol with hydrogen chloride in a freezing mixture, separating the upper layer of liquid and subjecting it to fractional distillation; it boils at 79—80°, with slight evolution of hydrogen chloride, and is readily decomposed by water. On treating it with anhydrous sodium acetate, reaction takes place easily, the *acetate*, $EtO\cdot CH_2\cdot OAc$, being formed; this is an oil of pleasant odour, is heavier than water, and boils at 130—131° under 738·6 mm. pressure. W. J. P.

Neutralisation of Glycerophosphoric Acid in Presence of Helianthin A and Phenolphthalein. By H. IMBERT and A. ASTRUC (*Compt. rend.*, 1897, **125**, 1039—1040).—Glycerophosphoric acid is acid to both helianthin A and to phenolphthalein. When neutralised with an alkali, it behaves as a monobasic acid in presence

of the former and as a dibasic acid in presence of the latter. The radicle, $CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, has affected only the alcoholic function of the phosphoric acid, and is without influence on either of the true acidic functions. C. H. B.

Aliphatic Nitroso-compounds. By OSCAR PILOTY (*Ber.*, 1898, 31, 218—220).—Victor Meyer, as the result of his researches on the action of nitrous acid on various aliphatic compounds (Abstr., 1888, 702) came to the conclusion that true nitroso-compounds are rarely if ever met with in the aliphatic series. The product obtained by Baeyer by the union of nitrosyl chloride with terpineol acetate (Abstr., 1894, i, 252), and by Thiele by the union of the same substance with tetramethylethylene (*ibid.*, i, 217) are undoubtedly to be regarded as true nitroso-derivatives, as also are Meyer's pseudo-nitroles. From these results, and from experiments previously conducted by the author on the action of benzenesulphonic chloride and alkali on hydroxylamine derivatives (Abstr., 1896, i, 555), the conclusion is drawn that only such compounds are capable of yielding true nitroso-derivatives which contain nitrogen attached to a tertiary carbon atom. The author has succeeded in obtaining aliphatic nitroso-derivatives from compounds containing the hydroxylamido- or nitro-groups attached to a tertiary carbon atom (see following abstract). All these nitroso-compounds are colourless in the solid state but give deep blue solutions.

J. J. S.

Aliphatic Nitroso-compounds. By OSCAR PILOTY and OTTO RUFF (*Ber.*, 1898, 31, 221—225. Compare preceding abstract).—When tertiary nitro-alcohols are reduced, or tertiary hydroxylamine derivatives are oxidised, a deep blue solution is always obtained and this probably contains the nitroso-compound; in no case, however, could such a compound be isolated. Aliphatic nitroso-compounds can readily be obtained by the oxidation of acetyl derivatives of tertiary hydroxylamido-alcohols with chromic anhydride. The compounds thus obtained are colourless but give deep blue solutions, and even fuse to blue liquids; they are volatile; their vapours have an odour of mustard oil and they give Liebermann's nitroso-colour reaction.

Tertiary triacetylnitroisobutylglycerol (triacetylmethylol-2-nitro-2-propandiol-1:3), $NO_2 \cdot C(CH_2 \cdot OAc)_3$, is obtained when nitroisobutylglycerol (Abstr., 1897, i, 4) is heated with three times its weight of acetic anhydride on the water bath and then boiled for $\frac{1}{4}$ hour; it crystallises from 95 per cent. alcohol in hard, rhombic prisms, melts at 74—75°, is only sparingly soluble in water or light petroleum, but dissolves more readily in ether, hot alcohol, acetic acid, or benzene. When it is reduced in ethereal solution with aluminium amalgam and water, *triacetylisobutyl-β-hydroxylamine* (triacetylmethylol-2-hydroxylamino-2-propandiol-1:3), $OH \cdot NH \cdot C(CH_2 \cdot OAc)_3$, is formed, and is best isolated in the form of its *oxalate*, $C_{12}H_{19}NO_{11} + \frac{1}{2}H_2O$, which crystallises from ethylic acetate in slender needles melting and decomposing at 95°; it dissolves readily in water and alcohol, but is only sparingly soluble in ethylic acetate and ether. *Nitrosotriacetylisobutylglycerol*, $NO \cdot C(CH_2 \cdot OAc)_3$, is obtained when the crude ethereal solution of the hydroxylamine derivative (from 10 grams of the nitro-compound) together with the

aluminium hydroxide is cooled to 0° and then oxidised with an ice-cold solution of potassium dichromate (3 grams) and concentrated sulphuric acid (5 c.c.) in water (300 c.c.); the mixture is well shaken for a few minutes in a separating funnel, the deep blue ethereal solution separated, washed 2—3 times with water, and the ether distilled; the residue, after recrystallisation from methylic alcohol, forms needles melting at 73° (corr.). It is sparingly soluble in water, readily in hot alcohol and moderately in benzene or acetic acid, and is decomposed when warmed with hydrochloric acid, yielding acetic acid, formaldehyde, and an amorphous compound.

Tertiarydiacetylnitropentandiol, $NO_2\cdot CEt(CH_2\cdot OAc)_2$, obtained from Pauwel's nitropentandiol, is a thick, colourless, odourless syrup boiling at 168° under a pressure of 22 mm.; it is practically insoluble in water but is readily miscible with alcohol or ether. *Diacetylnitrosopentandiol*, $NO\cdot CEt(CH_2\cdot OAc)_2$, crystallises from light petroleum in glistening, prismatic plates, melts at 71—72° (corr.) is sparingly soluble in benzene or ethylic acetate, and in odour resembles nitrosobenzene. *Diacetylnitrobutandiol*, $NO_2\cdot CMe(CH_2\cdot OAc)_2$, crystallises in compact needles, melts at 27—28°, and distils at 158° under a pressure of 20 mm., it is readily soluble in ether or alcohol, sparingly in light petroleum, and almost insoluble in water. The corresponding *nitroso*-compound $NO\cdot CMe(CH_2\cdot OAc)_2$, melts at 53° (corr.), is readily soluble in alcohol or ether, but only sparingly in light petroleum. J. J. S.

Action of Benzhydrazide on Glucose. By GEORG PINKUS (*Ber.*, 1898, **31**, 31—37).—The product described by Davidis as glucosebenzosazone, $OH\cdot CH_2\cdot CH(OH)\cdot[C(:N\cdot NHBz)]_3\cdot CH:N\cdot NHBz$ (Abstr., 1897, i, 5), and obtained by heating glucose with benzhydrazide and very dilute caustic soda for 1½ hours on the water bath, is shown to be a mixture of the benzosazones of glyoxal and methylglyoxal. When it is extracted repeatedly with large quantities of boiling alcohol, *glyoxal benzosazone*, $C_2H_2(:N\cdot NHBz)_2$, is left; an identical product is obtained from glyoxal and benzhydrazide; it decomposes at about 380°. The hot alcoholic extract deposits *methylglyoxalbenzosazone*, $C_2HMe(:N\cdot NHBz)_2$, on cooling; an identical product is obtained from benzhydrazide and either glycerose or methylglyoxal; it melts and decomposes at 251—252°. This substance is converted by heating with phenylhydrazine into methylglyoxal phenylosazone melting at 148°, which is also obtained when glucose is heated with phenylhydrazine and very dilute caustic soda.

It is not probable that the methylglyoxal is derived from glyceric aldehyde, which would be a primary product of the decomposition of glucose, for although this aldehyde (glycerose: see above) reacts with benzhydrazide in weak acetic acid solution, yielding methylglyoxal benzosazone, the reaction is extremely slow in alkaline solution. More probably, the methylglyoxal is derived from acetol, $CH_3\cdot CO\cdot CH_2\cdot OH$, for this reacts with benzhydrazide in alkaline solution, yielding methylglyoxal benzosazone; with phenylhydrazine in acetic acid solution, it yields acetolphenylhydrazone (Laubmann, Abstr., 1888, 366), which has now been obtained crystalline, and melts at 100—102°.

Methylglyoxal is formed from dihydroxyacetone (Piloty, this vol., i.,

117), when the latter is distilled with dilute sulphuric acid, for the distillate yields methylglyoxal phenylosazone when it is treated with phenylhydrazine. C. F. B.

Action of Boiling Water on d-Fructose (Levulose). By CORNELIS ADRIAAN LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1897, **16**, 282—283).—In order to ascertain whether any transformation occurs when sugars are heated with water alone, fructose was boiled with water in a platinum reflux apparatus for 80 hours. Beyond a slight diminution in the specific rotatory power of the fructose, no other change was observed. A. R. L.

Production and Occurrence of Levulose in Factory Products. By H. C. PRINSEN (*Bied. Centr.*, 1897, **26**, 767—770; from *Arch. Java-Suikerind.*, 1896, Afl. 7).—In reply to Pellet, who states that levulose is precipitated by basic lead acetate (*Bull. Assoc. Chimistes*, 1896, 562), the author shows that lead acetate does not precipitate levulose. The rotatory power is slightly altered in alkaline solutions, but is restored by a drop of acetic acid. In presence of substances which are precipitated by basic lead acetate, the precipitate carries down the levulose; this occurs only when basic lead acetate is employed, and there is no precipitation of levulose with normal lead acetate in neutral or acid solutions. Dextrose is not precipitated.

With regard to factory products, which are usually neutral, polariscope results are not trustworthy. In molasses, levulose and dextrose are present in equal amounts, owing to changes during the processes of manufacture. Levulose could not be detected in ripe canes. In analysing such products, normal lead acetate should be employed, together with fine animal charcoal.

When a 10 per cent. dextrose solution is heated at 100° with sodium or potassium acetate (Na_2O or $K_2O = 2·5$ per cent.), the rotatory power is reduced to less than half in 4 hours, whilst the amount of reducing substance remains about the same. This explains the presence of lævorotatory glucose in molasses originally dextrorotatory in the juice. (compare *Zeits. Ver. Rübenzuckerind.*, 1895, 320, and de Bruyn and Alberda van Ekenstein, Abstr., 1896, i, 116). The results indicate that, in plants, the production of levulose from dextrose may be effected by salts of organic acids instead of by free bases as has been assumed. Ordinary cane-sugar molasses was found to contain, besides saccharose, dextrose and levulose in about equal amounts, and almost 5 per cent. of mannose. The mannose can only have been produced during the treatment in the factory. N. H. J. M.

Action of Alkalis on the Sugars. IV. By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1897, **16**, 257—261).—General remarks on the papers following.
A. R. L.

Action of Alkalis on the Sugars. V. Transformation of Galactose. The Tagatoses and Galtose. By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1897, **16**, 262—273).—When a 20 per cent. aqueous solution of galactose is

heated at 70° for 3 hours with 3 per cent. (on the sugar) of potassium hydroxide, the rotatory power sinks to $[\alpha]_D = +37 \cdot 5°$, and the solution contains about 50 per cent. of unaltered galactose, which can, for the most part, be removed by crystallisation. The residual syrup is mixed with a little methylic alcohol and extracted with acetone. On evaporating the solvent, a syrup is obtained containing a little galactose, and other reducing sugars, namely, *d*-tagatose, *ψ*-tagatose, galtose, and *d*-talose. The galactose is precipitated as methylphenylhydrazone, or is removed by fermentation with yeast.

d-*Tagatose*, $C_6H_{12}O_6$, crystallises from water and melts at 124°. The specific rotatory power is $[\alpha]_D = +1°$, and this becomes $-2 \cdot 6°$ at 60°. Like fructose, it is decomposed by dilute acids, and gives an intense reddish-violet coloration with hydrochloric acid and resorcinol; it is unfermentable with yeast. When treated with alkalis, about 10 per cent. is transformed into galactose. It forms an amorphous compound with acetone (2 mols.), which has a rotatory power of $[\alpha]_D = +50°$ (about). The *osazone* melts at 193°, and its solutions are optically inactive.

ψ-Tagatose, $C_6H_{12}O_6$, separates from water, in which it is less soluble than *d*-tagatose, in well-defined crystals which melt at 156°. The specific rotatory power of a 2 per cent. and 6 per cent. solution is $[\alpha]_D = +33 \cdot 4°$ and $+35°$ respectively, and these values remain unaltered when the temperature is raised to 60°. The aqueous solution is perceptibly sweet. Its behaviour towards dilute acids and with hydrochloric acid and resorcinol is the same as that of *d*-tagatose, but it is slowly fermentable with yeast. When treated with alkalis, about 14 per cent. is transformed into galactose. The *osazone* melts at 140°, dissolves in 333 parts of boiling water, and its solution in acetic acid has a rotatory power of $[\alpha]_D = +21°$.

Both *d*- and *ψ*-tagatose resemble fructose in their indifference towards iodine and bromine; the authors did not succeed in preparing acetyl derivatives from these sugars.

Galtose, $C_6H_{12}O_6$, is present in the mother liquor from which the sugars just described are isolated, but is best prepared by heating a 20 per cent. solution of galactose with lead hydroxide (10 per cent. on the sugar). After removing the lead salts, first with alcohol and then by precipitation with an alcoholic solution of tartaric acid, the galactose is eliminated by fermentation with yeast; a syrup is finally obtained consisting of galtose with a little *d*-talose. Galtose, which has not yet been obtained in a crystalline form, is unfermentable with yeast, optically inactive, and has an indistinctly sweet taste. It yields acids, but no galactose, when treated with alakalis. The *osazone* is soluble in 500 parts of boiling water, and melts at 182°; the rotatory power of a solution in methylic alcohol is $[\alpha]_{Auer} = +19°$. The sugar, like the ketoses, is unstable towards dilute acids, but its reducing power towards Fehling's and Romijn's (iodine) solution is about half that of the better-known aldoses. It yields about 4—5 per cent. of furfuraldehyde when distilled with hydrochloric acid.

d-Talose is only formed in these transformations in very small amount (at most 8 per cent.), and although it can be precipitated as the naphthylhydrazone, or 1 : 4-nitrophenylhydrazone, the precipitation is incomplete. Talose mixed with organic acids may be prepared by

decomposing the other sugars in the transformation products by means of acids. The authors have not, therefore, succeeded in crystallising talose. A. R. L.

Action of Alkalis on the Sugars. VI. Glutose and ψ-Fructose. By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1897, **16**, 274—281).—*Glutose*, $C_6H_{12}O_6$, is invariably formed when the three sugars, glucose, mannose, and fructose are transformed reciprocally into one another. It is best prepared by heating a 20 per cent. solution of fructose at 100° with lead hydroxide (10 per cent. on the sugar). After removing the lead salt, the product is fermented with yeast, when glutose remains in the form of a syrup; the authors have not yet succeeded in obtaining it in a crystalline form. It is optically inactive, and in this and several other properties resembles galtose (preceding abstract); the *osazone*, however, is soluble in 200 parts of boiling water, melts at 165°, and a solution in methylic alcohol has a rotatory power of $[\alpha]_{Auer} = +6°$.

There is some evidence that when glucose, mannose, or fructose is heated with alkali hydroxides, a fifth sugar, a ketose, which may be denoted *ψ-fructose*, is present among the products. Thus, if an attempt be made to estimate the fructose in the mixture of sugars, it would appear that the sugar present has a lower lævorotation than ordinary fructose, and this is also confirmed by directly observing the rotatory power of the supposed fructose regenerated from the insoluble lime compound obtained from the same mixture. The view that ψ-fructose is present is also supported by the fact that the authors have isolated a new osazone from the mixture, which melts at 160° and, when dissolved in methylic alcohol, has a rotatory power of $[\alpha]_{Auer} = -5·3°$.

The authors have previously drawn attention to the occurrence of mannose in the molasses obtained from the products of the sugar cane, this sugar being formed by the action of lime, with which the cane juice is boiled, on the invert-sugar. They now show that such molasses contains also glutose, the amount of which may be approximately estimated by fermenting the molasses with yeast, and subsequently determining the reducing power of the residue before and after treatment with hydrochloric acid according to the Sieben-Dammüler method. In this way, a sample of Louisiana molasses was shown to contain 4·8 per cent. of glutose, whilst 2·6 per cent of the same sugar was found in a sample of Egyptian molasses. The Louisiana molasses also contained 0·4 per cent. of mannose. A. R. L.

Nitration of Carbohydrates. By WILHELM WILL and FRIEDRICH LENZE (*Ber.*, 1898, **31**, 68—90).—In order to throw light on the nature of the bye-products arising from the nitration of cellulose, the authors have investigated the behaviour of various carbohydrates towards a mixture of concentrated nitric and sulphuric acids, it having been observed that cellulose is resolved into sugar under the influence of dilute acids. The nitrates obtained by this means are readily oxidised by Fehling's solution, and rotate the plane of polarised light; they dissolve in acetone, acetic acid, and alcohol, but are insoluble in water and petroleum. They do not dissolve in cold, concentrated hydro-

chloric acid, and undergo decomposition when the liquid is heated, chlorine being set free; boiling water gradually decomposes them, eliminating oxides of nitrogen, with slow dissolution of the product.

Rhamnose tetranitrate, $C_6H_8O_5(NO_2)_4$, separates from alcohol in colourless, rhombic crystals and melts at 135°, decomposing at 136°; a 2·3 per cent. solution in methylic alcohol has $[\alpha]_D = -68·4°$.

Arabinose tetranitrate, $C_5H_6O_5(NO_2)_4$, is deposited by alcohol in monoclinic crystals and melts at 85°, decomposing at 120°; a freshly prepared 4·4 per cent. solution in alcohol has $[\alpha]_D = -101·3°$, which drops to $-90°$ after 20 hours.

Xylose anhydride dinitrate, $C_5H_6O_4(NO_2)_2$, crystallises from alcohol in spherical aggregates and melts at 75—80°.

Glucose pentanitrate, $C_6H_7O_6(NO_2)_5$, is an amorphous powder which melts at 10°, decomposing at 135°; it dissolves very readily in alcohol, and is insoluble in water and petroleum. In a 6 per cent. alcoholic solution, it has $[\alpha]_D = 98·7°$; it reduces Fehling's solution when heated with it.

Galactose pentanitrate, $C_6H_7O_6(NO_2)_5$, occurs in two forms. The α-modification dissolves less readily in alcohol, from which it crystallises in slender, transparent needles, and melts at 115—116°, decomposing at 126°; a 4 per cent. solution in alcohol has $[\alpha]_D = 124·7°$. The β-compound crystallises in monoclinic needles, melts at 72—73°, and decomposes at 125°; a 6·7 per cent. solution in alcohol has $[\alpha]_D = -57°$.

Mannose pentanitrate crystallises from absolute alcohol in transparent, rhombic needles, melts at 81—82°, and decomposes at 124°; a 5 per cent. solution has $[\alpha]_D = 93·3°$.

Lævulosan trinitrate, $C_6H_7O_5(NO_2)_3$, is produced in two distinct forms. The α-modification crystallises from alcohol in lustrous needles, melts at 137—139°, and decomposes at 145°; a 1 per cent. solution in methylic alcohol has $[\alpha]_D = +62°$. The β-compound crystallises in spherical aggregates, melts at 48—52°, and decomposes at 135°; a 5 per cent. solution in alcohol has $[\alpha]_D = 20°$.

Sorbinosan trinitrate, $C_6H_7O_5(NO_2)_3$, melts indefinitely at 40—45°.

α-Glucoheptose hexanitrate, $C_7H_8O_7(NO_2)_6$, crystallises from alcohol in transparent needles and melts at 100°; a 3·4 per cent. solution in alcohol has $[\alpha]_D = +104·8°$.

α-Methylglucoside tetranitrate, $C_7H_{10}O_6(NO_2)_4$, crystallises from alcohol in lustrous, quadratic plates, melts at 49—50°, and decomposes at 135°; a 6·2 per cent. solution in alcohol has $[\alpha]_D = 140°$.

Methyl-d-*mannoside tetranitrate* crystallises from alcohol in slender needles resembling asbestos and melts at 36°; a 2·5 per cent. solution in alcohol has $[\alpha]_D = 77°$.

Saccharose octonitrate, $C_{12}H_{14}O_{11}(NO_2)_8$, crystallises in spherical aggregates, melts at 28—29°, and decomposes at 135°; a 3·4 per cent. solution in alcohol has $[\alpha]_D = 52·2°$.

Lactose octonitrate, $C_{12}H_{14}O_{11}(NO_2)_8$, crystallises from alcohol in leaflets and melts at 145—146°; a 2·8 per cent. solution in methylic alcohol has $[\alpha]_D = 74·2°$. This compound closely resembles the pentanitrate described by Gélis. The *hexanitrate* melts at 81°.

Maltose octonitrate, $C_{12}H_{14}O_{11}(NO_2)_8$, crystallises from alcohol in

lustrous needles, and melts and decomposes at 163—164°; a 3·5 per cent. solution in glacial acetic acid has $[\alpha]_D = 128·6$.

Trehalose octonitrate crystallises from alcohol in nacreous leaflets, melts at 124°, and decomposes at 136°; a 4 per cent. solution in glacial acetic acid has $[\alpha]_D = 173·8°$.

Raffinose undecanitrate, $C_{18}H_{21}O_{16}(NO_2)_{11}$, separates from alcohol in amorphous, spherical aggregates, melts indefinitely at 55—65°, and decomposes at 136°; a 3·6 per cent. solution in alcohol has $[\alpha]_D = +94·9°$.

β-Glucosan trinitrate, $C_6H_7O_3(NO_2)_3$, crystallises from alcohol in lustrous needles and melts at 101°; a 2·4 per cent. solution in alcohol has $[\alpha]_D = -61·4°$.

A hexanitro-derivative of starch, $C_{12}H_{14}O_{10}(NO_2)_6$, is an amorphous powder which decomposes at 194° without previously melting (compare Mühlhäuser, Abstr., 1893, i, 6).

Wood gum also yields a nitro-derivative (compare Bader, Abstr., 1896, i, 335). M. O. F.

Carbohydrates contained in the Corm of Cyclamen Europæum. By Bohuslav Rayman (*Chem. Centr.*, 1897, i, 230—231; from *Rozpravy české akademie*, 1896, Cl. 2, Nr. 30).—Cyclamose and cyclamin are obtained from the corm by extracting it with 70 per cent. alcohol, and may be separated by means of absolute alcohol in which the latter is soluble. *Cyclamin*, $C_{27}H_{38}O_{13}$, which is purified by precipitating it from a concentrated aqueous solution by ether, gives a dark red coloration with fuming sulphuric acid; the aqueous solution froths like that of saponin, but is more easily decomposed by acids or by boiling. By the action of sulphuric acid, it is decomposed into cyclamiretin, $C_{14}H_{18}O_2$, levulose, and a dextrorotatory sugar, *cyclose*. *Cyclamiretin* yields an amorphous bromine additive compound, a benzoate, and an acetate. Cyclamose, $C_{36}H_{62}O_{31}$, which the author proposes to name *cyclamosin*, is a white, amorphous powder, has a sweetish taste, deliquesces, and becomes black on exposure to the air, and with hydrochloric acid yields levulose.

No mannitol could be detected, and the residue left after extracting with alcohol consists of starch and cellulose. E. W. W.

Pentosans in the Beet Sugar Manufacture. By K. Komers and Anton Stift (*Bied. Centr.*, 1897, **26**, 861; from *Oesterr. Zeit. Zuckerind.*, 1897, 627).—In purifying beetroot sap in the usual manner, most of the pentosans are removed and are probably converted by the action of the lime into more or less complex, insoluble compounds which would be retained in the deposit. A part of the pentosans pass to the green syrup and from this to other products; only a slight amount is to be found in the molasses. A portion of the pentosans remains in the crude sugar and it is very likely that they form a not inconsiderable portion of the organic impurity present in crude sugar. The reducing action of many crude sugars is perhaps due in part to the presence of pentosans as well as to invert-sugar. N. H. J. M.

The Conversion of Starch by means of Sulphurous Anhydride and Sulphurous Acid. By A. Bergé (*Bied. Centr.*, 1897, **26**, 863; from *Zeit. Spir. Ind.*, 1897, 206).—Liquid sulphurous anhydride

converts dry starch first into soluble starch and then into dextrin when heated above 80°. Below this temperature, there is no action, whilst at temperatures slightly above 115°, soluble starch is the chief product. Sulphurous acid has no effect on starch below 45°; at 100°, the starch dissolves, whilst at a temperature not above 115° (with 1 per cent. sulphurous acid) a gummy product is obtained consisting of a little soluble starch and dextrins with 5 to 10 per cent. of dextrose. At 135—140°, the starch is converted entirely into dextrose; this change is best effected by heating starch (25 per cent.) and 3—6 per cent. sulphurous acid (75 per cent.) for an hour at 140°.

N. H. J. M.

Precipitation of Carbohydrates by Neutral Salts. By Robert Arthur Young (*J. Physiol.*, 1898, **22**, 401—422).—The salt precipitation (salting out) method can be quite as easily applied to the separation of colloid carbohydrates as to proteids. Ammonium sulphate, magnesium sulphate, and sodium sulphate (at 33°, the temperature of its greatest solubility) are the most generally useful salts, but the crystalline carbohydrates cannot be precipitated by this method. Starch and soluble starch are both readily precipitable by salts. The erythrodextrins are quite distinct from either starch or the achroodextrins, a fact entirely in opposition to the views of Musculus and Meyer and of Ost. Of these substances, two are precipitable by salts and one is not; these three substances, distinguished as erythrodextrin i, ii, and iii, give reactions closely similar to the products obtained by Lintner and Düll by other methods. The main bulk of the achroodextrins is not precipitable by this means. Glycogen is readily and completely precipitated by saturation with ammonium sulphate, or by sodium sulphate at 33°, and is thus readily distinguished from erythrodextrin iii. Inulin is partly precipitated from its solutions by salts, especially by magnesium sulphate. All the soluble iodine compounds of starch, soluble starch, and the erythrodextrins are precipitated by salts more readily than the original carbohydrate. The colour of the iodine compounds varies with the concentration of the iodine. Soluble starch gives a blue coloration with iodine under all conditions, and has a greater attraction for iodine than the erythrodextrins. Erythrodextrin i gives a reddish-purple with iodine after the removal of all soluble starch. There is no evidence as to the existence of a combination of the colloid precipitated and the salt precipitating, neither does the precipitating, or water-attracting, power of a salt depend on its molecular weight or its solubility. W. D. H.

Hydrolysis of Glycogen. By M. Christine Tebb (*J. Physiol.*, 1898, **22**, 423—432).—In the hydrolysis of glycogen, produced by mineral acids, intermediate substances of the dextrin class are formed which may be termed soluble glycogen, erythrodextrin, and achroodextrin. The final sugar formed is dextrose (identified by its osazone) and prolonged hydrolysis converts all the intermediate dextrins into sugar.

The intermediate dextrins may be separated by fractional precipitation with alcohol, and also by Young's salt saturation method (preceding abstract); this is a valuable means of discriminating between

erythrodextrin on the one hand, and glycogen and soluble glycogen on the other.

In the hydrolysis of glycogen, produced by the amylolytic enzymes of saliva, pancreatic extract, and malt extract, the only dextrins which could be separated in amount sufficient to work with subsequently are of the achroo-variety; small quantities of erythrodextrin were sometimes obtained, but these early products of the hydrolytic process are very rapidly changed. In the case of the liver enzyme, the results are similar, except that erythrodextrin is more constantly found; the liver enzyme differs from the others in the nature of the final product, which is dextrose, not maltose. By the prolonged action of all these enzymes, a form of achroodextrin (called by Seegen dystropo-dextrin) is produced which resists further conversion into sugar; this requires for its precipitation a larger percentage of alcohol than that required for the precipitation of the achroodextrin formed in an earlier stage of the hydrolysis. W. D. H.

Chemistry of the Barley Plant with Reference to its Carbohydrate Constituents. By CHARLES F. CROSS and EDWARD J. BEVAN (*J. Fed. Inst. Brew.*, 1897, **3**, 2—18).—In this paper, an account is given of the results which have been obtained by the authors in so far as they relate to the nature of the furfuraldehyde-yielding carbohydrates of the barley plant.

Seeing that the "spent grains" of the brewery contain considerable proportions of these carbohydrates, and that the latter, on acid hydrolysis, yield substances which are partially fermentable by yeast, it is suggested that these grains might be utilised by the brewer as an additional source of alcohol and extractive matter. Boiling for 2 hours in an open vessel with 1 per cent. sulphuric acid was found to be sufficient for their hydrolysis. A sample of malt-wort having a sp. gr. = 1·0944, to which the extract from the spent grains (furfuroids) had been added, fermented down to 1·018 after the addition of yeast.

A. C. C.

Tetrallylammonium Alum. By N. A. ORLOFF (*Chem. Centr.*, 1897, i, 1156; from *Pharm. Zeit. Russ.*, **36**, 212—213. Compare Abstr., 1896, i, 634, and 1897, i, 448).—Tetrallylammonium alum, $N(C_3H_5)_4Al(SO_4)_2 + 12H_2O$, crystallises in octahedra, and is very slightly soluble in water, whereas the anhydrous salt is easily soluble in water; the whole of the sulphuric anhydride cannot be expelled by heating in the Bunsen flame. Tetrallylammonium iodide, when dissolved in an equal weight of water, lowers the temperature 7°.

E. W. W.

Methylation of Hydrazine Hydrate. By CARL D. HARRIES and TAMEMASA HAGA (*Ber.*, 1898, **31**, 56—64. Compare von Rothenburg, Abstr., 1893, i, 410).—*Trimethylazonium iodide*, $NH_2 \cdot NMe_3I$, is obtained by agitating an aqueous solution of hydrazine hydrate with methylic iodide and caustic potash; it dissolves readily in water, and is somewhat soluble in boiling ethylic and amylic alcohols. It melts and decomposes at about 235°, and resembles ammonium chloride in crystalline structure. The *chloride* is hygroscopic, and the *hydroxide*

is an alkaline solid which absorbs carbonic anhydride and does not reduce Fehling's solution. When the hydroxide is submitted to distillation, it is resolved into methylic alcohol and unsymmetrical dimethylhydrazine, the *oxalate* of which crystallises in elongated plates and melts at 142—143°; dimethylamine is also produced. Agitation with methylic iodide and caustic potash converts trimethylazonium hydroxide into the iodide, and when the latter is heated with methylic iodide and methylic alcohol in a sealed tube at 125—130°, it yields tetramethylammonium iodide and a mixture of inflammable gases.

In the absence of caustic potash, the action of methylic iodide on hydrazine hydrate gives rise to a mixture of methylhydrazine and unsymmetrical dimethylhydrazine when excess of the base is employed; if methylic iodide is in excess, however, hydrazine hydriodide, trimethylazonium iodide, and methylhydrazine hydriodide are produced. Methylhydrazine *oxalate* crystallises from dilute alcohol in slender needles and melts at 166°.

Tribenzylidenemethylhydrazine, $(CHPh{:}N{\cdot}NMe)_2CHPh$, prepared from methylhydrazine (2 mols.) and benzaldehyde (3 mols.), crystallises from light petroleum in slender, white needles and melts at 109°. The substance does not reduce Fehling's solution, but is resolved into its components by hot dilute hydrochloric acid.

Benzylidenemethylhydrazine, $CHPh{:}N{\cdot}NHMe$, is also obtained from methylhydrazine and benzaldehyde (1 mol.), and crystallises from alcohol in thick plates melting at 179°.

Symmetrical dimethylhydrazine (Harries and Klamt, Abstr., 1895, i, 262) can be prepared by acting on potassium diformylhydrazine with methylic iodide. The *oxalate* crystallises from absolute alcohol in flattened prisms, and melts at 132°; it reduces Fehling's solution when heated. M. O. F.

Hydrolysis of Sylvan to Levulinaldehyde (Constituents of Beech-wood Tar. I.). By CARL D. HARRIES (*Ber.*, 1898, 31, 37—47).—The sylvan (methylfurfuran) obtained by Atterberg (Abstr., 1880, 663) from the tar-oil of *Pinus sylvestris*, is also contained in beech-wood tar; it is shown to be 2-methylfurfuran, $O{<}{\begin{matrix}CH{=}CH\\ CMe{:}CH\end{matrix}}$, by its ready conversion into levulinaldehyde. When 150 kilos. of beech-wood tar are distilled, 10 kilos. of the distillate come over below 70°; this fraction is exhausted successively with 40 per cent. sodium hydrogen sulphite and 10 per cent. caustic soda solutions; the residual oil (about 5 kilos.) is fractionated with a long Le Bel column, and the fraction boiling at 60—70° (1·4 kilos.) is boiled with fresh quantities of sodium until no further action takes place; the residual liquid (1 kilo.) is again distilled, when the sylvan (β-methylfurfuran) comes over at 65° under 759 mm. pressure (850 grams); it has sp. gr. = 0·827 at 18°/18°.

When sylvan (500 grams) is boiled with methylic alcohol (1500 c.c.) and 80 per cent. methylic alcoholic hydrochloric acid (20 grams) for 24 hours, levulinmethylal is formed, together with a polymeride which boils at 180—220° under 10 mm. pressure, and is also formed when the methylal is allowed to remain with small quantities of acid.

Levulinmethylal, $CMeO\cdot CH_2\cdot CH_2\cdot CH(OMe)_2$, boils at 87—88° under 17 mm. pressure, at 79—80° under 13 mm.; its sp. gr. = 0·9684 at 18°/18°; it yields an oily oxime, and an oily phenylhydrazone which slowly changes into phenylmethyldihydropyridazine (see below). *Levulinacetal*, $CMeO\cdot CH_2\cdot CH_2\cdot CH(OEt)_2$, is formed when ethyl alcoholic, instead of methyl alcoholic, hydrochloric acid is used; it boils at 92—93° under 11—12 mm. pressure. *Levulinaldehyde*,

$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CHO,$$

is formed when the methylal is boiled for a few minutes with 2 per cent. hydrochloric acid, the acid then neutralised with sodium hydrogen carbonate, and the aldehyde salted out with potassium carbonate, the precaution being taken to cover the aqueous solution with a layer of ether and shake after each addition of potassium carbonate. It boils at 70° under 12 mm. pressure, at 66° under 8·5 mm.; under atmospheric pressure, it boils at 186—188° with slight decomposition; it has a sp. gr. = 1·0156 at 16°, and mixes with water in all proportions. Silver oxide oxidises it to levulinic acid; with ammonia, in ethereal solution, it forms a crystalline precipitate which is converted into 2-methylpyrroline by boiling with aqueous acetic acid; with phenylhydrazine acetate in aqueous solution, it yields *phenylmethyldihydropyridazine*, $NPh{<}\begin{matrix}N{=\!=}CH\\CMe{:}CH\end{matrix}{>}CH_2$, which melts and decomposes at 197°; it also forms a *dioxime* melting at 67—68°, a crystalline *semicarbazone*, and a crystalline compound with 2 mols. of sodium hydrogen sulphite.

C. F. B.

Constitution of Pinacolin. By CÆSAR POMERANZ (*Monatsh.*, 1897, **18**, 575—581).—The results recently obtained by Delacre (Abstr., 1896, i, 591, and i, 662) are in favour of the symmetrical formula, $O{<}\begin{matrix}CMe_2\\|\\CMe_2\end{matrix}$, of Friedel and Silva for pinacolin. Accepting this, the trimethylpyruvic acid obtained by Glücksmann (Abstr., 1892, 38) on oxidising pinacolin, would have the formula $O{<}\begin{matrix}CMe_2\\|\\CMe\cdot COOH\end{matrix}$, and to the hydroxy-acid obtained by reducing this, the formula

$$CHMe_2\cdot CMe(OH)\cdot COOH$$

would be given, since, on being heated with sulphuric acid, it loses carbonic oxide and water, and yields methyl isopropyl ketone. The author has, however, prepared *hydroxymethylisopropylacetic acid* from methyl isopropyl ketone and hydrocyanic acid, by the method of Wislicenus and Urech; it crystallises from water, melts at 63°, is easily soluble in alcohol and ether, and is not identical with Glücksmann's hydroxy-acid. The symmetrical formula for pinacolin is therefore untenable.

The author confirms Butleroff's statement that the acid $C_5H_{10}O_2$, obtained on oxidising pinacolin, is identical with synthetical trimethylacetic acid; both acids melt at 34—35°, boil at 163°, and, in solutions of equal concentration, possess the same molecular conductivity. The calcium salts are also identical, crystallising with $4H_2O$, and not with $5H_2O$, as stated by Butleroff.

W. A. D.

Derivatives of Pinacolin. By E. CARLINFANTI (*Gazzetta*, 1897, 27, ii, 387—392).—In the hope of obtaining an acid of the constitution $CMe_3 \cdot CHMe \cdot COOH$, the author has prepared *pinacolin cyanhydrin*, $CMe_3 \cdot CMe(OH) \cdot CN$, by treating a mixture of pinacolin and potassium cyanide with hydrochloric acid at 0°; on fractionally distilling the product, a small yield of the cyanhydrin was obtained as an unstable, white, crystalline substance melting at 82—87° which has the normal molecular weight in freezing benzene. On hydrolysis with dilute potash, sulphuric acid, hydrochloric acid, or hydrogen peroxide, it yields pinacolin instead of the carboxylic acid.

Pinacolinsemicarbazone, $C_7H_{15}N_3O$, which is readily prepared, crystallises in lustrous, white needles melting at 175°. Pinacolin reacts with phenylhydrazine and parabromophenylhydrazine, yielding resinous products. W. J. P.

Determination of Acetyl Groups in Organic Compounds. By FRANZ WENZEL (*Monatsh.*, 1897, 18, 659—672).—The author points out the limitations of methods at present in use, and describes a process which is universally applicable. It consists in hydrolysing the acetyl compound with dilute sulphuric acid (2 acid : 1 water), and distilling the acetic acid formed into decinormal potash. The distillate should be free from sulphurous acid when titrated against decinormal iodine; if this is not the case, the sulphuric acid used for hydrolysis must be diluted. In the case of sulphur compounds, in order to prevent error by the liberation of hydrogen sulphide, cadmium sulphate is mixed with the substance before hydrolysis; if the compound contains a halogen, silver sulphate must be added.

To carry out the process, 0·2—0·4 gram of the compound is placed in a distilling flask connected with a short reflux condenser, the further end of which is bent so as to pass down into a second smaller distilling flask. The side tube of this flask is connected to the upper end of a vertical condenser; this dips into decinormal potash contained in a pump-flask, in which a vacuum can be produced. Three c.c. of the dilute sulphuric acid is added to the acetyl compound, and, after some time, 3 c.c. of water; the mixture is then heated at 60—70° until complete hydrolysis is effected. Twenty c.c. of a solution containing 100 grams of metaphosphoric acid and 450 grams of crystallised disodium phosphate in a litre of water are then added, the flask is connected with a hydrogen generating apparatus, and the liquid distilled to dryness under greatly reduced pressure. Twenty c.c. of water is added and the distillation repeated. The second distilling flask serves to prevent traces of phosphoric acid being carried over into the decinormal alkali; during the distillation, it is heated in water to the same temperature as the flask containing the hydrolysed compound. After the second distillation, the apparatus is filled with hydrogen, the pump-flask and its condenser disconnected, and the excess of alkali determined by titration. The author has verified the accuracy of his method by the analysis of 41 acetyl compounds of widely differing constitution. W. A. D.

V. Meyer's Etherification Law. By ANGELO ANGELI (*Real. Accad. Linc.*, 1896, [v], 5, i, 84—88).—V. Meyer considers that, in

the action of an alcohol, $R'\cdot OH$, on an acid, $CR_2\cdot COOH$, in presence of hydrogen chloride, water is directly eliminated from the alcohol and acid with formation of the salt $CR_2\cdot COOR'$. The author considers the change to be of a more complex character and to involve the intermediate formation of compounds of the constitution $CR_2\cdot C(OH)_2\cdot OR'$ or $CR_2\cdot C(OH)(OR')Cl$. Evidence is quoted in favour of this view, which is also applied to other reactions, such as those involved in the formation of nitriles and oximes. W. J. P.

Hydrazidoacetic Acid. By WILHELM TRAUBE and E. HOFFA (*Ber.*, 1898, **31**, 162—169. Compare Abstr., 1897, i, 138).—Pure hydrazidoacetic acid is best obtained by the following method. *o*-Hydroxybenzylidenehydrazidoacetic acid is suspended in water, treated with sulphuric acid (1 mol.), and subjected to steam distillation until no more salicylaldehyde passes over; the sulphuric acid is precipitated with baryta water, the excess of the latter removed by warming with ammonium carbonate, the filtrate evaporated under diminished pressure, and the syrupy residue rubbed with alcohol; the crystalline mass is then dissolved in water and dropped into absolute alcohol. After this operation has been repeated several times, the purified acid is obtained in the form of needles melting at 152°. It dissolves readily in water, but is insoluble in alcohol, ether, or benzene, readily reduces Fehling's solution, and gives salts with mineral acids but not with bases. The *hydrochloride* of the ethylic salt, $NH_2\cdot NH\cdot CH_2\cdot COOEt,HCl$, obtained in the usual manner, crystallises from alcohol in glistening plates melting at 153°, and is readily soluble in water. The ethylic salt itself was only obtained as an oil.

Ethylic dibenzoylhydrazidoacetate, $NBz_2\cdot NH\cdot CH_2\cdot COOEt$, which crystallises from alcohol in needles melting at 113°, is readily soluble in alcohol, ether, or benzene, and does not reduce Fehling's solution. When hydrolysed by alkalis, it gives metallic salts of the dibenzoylated acid.

The three products, *ethylic carbamidohydrazidoacetate*,

$$NH_2\cdot CO\cdot NH\cdot NH\cdot CH_2\cdot COOEt,$$

ethylic amidohydantoate, $NH_2\cdot CO\cdot N(NH_2)\cdot CH_2\cdot COOEt$, and amidohydantoin, $\begin{matrix}CH_2\cdot N(NH_2)\\ | \\ CO\text{———}NH\end{matrix}\!>\!CO$, are obtained when the hydrochloride of ethylic hydrazidoacetate is treated with an excess of potassium cyanate in aqueous solution; after remaining for some time, the solution is evaporated to dryness under diminished pressure, and the residue extracted with hot alcohol until the extract no longer reduces Fehling's solution. The solid residue obtained when the alcoholic solution is evaporated under reduced pressure is extracted with large quantities of hot benzene, and on cooling ethylic carbamidohydrazidoacetate is deposited in the form of slender needles melting at 122°. The benzene mother liquor from these crystals yields ethylic amidohydantoate, which crystallises in colourless prisms melting at 70—74°. It is readily soluble in water, like its isomeride, but only reduces Fehling's solution after boiling for some time. It yields a *benzylidene* derivative which crystallises in needles melting at 150°.

The portion of the solid residue which is insoluble in benzene is dissolved in water, and the solution, when acidified and treated with

benzaldehyde, yields *benzylideneamidohydantoin* melting at 244°. A better yield of this compound is obtained when the solid residue produced in the reaction of ethylic hydrazidoacetate with an excess of potassium cyanate is hydrolysed with dilute sulphuric acid and the solution then shaken with benzaldehyde; the benzylidene derivative is somewhat difficult to hydrolyse. *Amidohydantoin hydrochloride* melts at 203°, is readily soluble in water, sparingly in alcohol.

When a solution of phenyl thiocarbamate (1 mol.) in alcohol is added to an aqueous solution of hydrazidoacetic acid (1 mol.) and potassium hydroxide (1 mol.), and the mixture warmed for a few minutes on the water bath, and, after cooling, mixed with absolute alcohol, *potassium* phenylthioamidohydantoate separates in crystals; it melts at 190°, is very readily soluble in water, and on the addition of hydrochloric acid yields *phenylthioamidohydantoic acid*,

$$NHPh\cdot CS\cdot N(NH_2)\cdot CH_2\cdot COOH,$$

which crystallises in needles, is moderately soluble in water, and melts at 135°. The acid yields a *benzylidene* derivative melting at 245°, and when heated with water at 103° loses carbonic anhydride, yielding *phenylthioamidohydantoin*, which melts at 165°. *Methylthioamidohydantoin* melts at 120°. J. J. S.

Action of Chlorine on Isovaleric Acid. By CLEMENTE MONTEMARTINI. (*Gazzetta*, 1897, **27**, ii, 368—374).—On passing chlorine into isovaleric acid at 90°, absorption occurs rapidly in sunlight, but very slowly in its absence; when the weight of the flask indicates that sufficient chlorine has been absorbed to form a monochloroderivative, the product is converted into an ethylic salt and *ethylic β-chlorisovalerate* may then be isolated by fractional distillation. It boils at 101—103° under 30 mm. pressure, and at ordinary pressures, with slight decomposition at 184—190°; it is heavier than, and insoluble in, water. The monochloro-derivative is accompanied by smaller quantities of a dichloro-derivative. Ethylic β-chlorisovalerate does not react with potassium cyanide, silver cyanide, or ethylamine, but converts silver hydroxide partly into chloride and partly into metal; it condenses with ethylic malonate, but no definite compound could be isolated from the product. The ethylic salt does not react satisfactorily with phenylhydrazine, but on heating the crude acid obtained by chlorination, with phenylhydrazine, a violent action occurs and on treatment with water and ether a *phenyldimethylpyrazolidone*,

$\begin{matrix} CMe_2\cdot NPh \\ | \\ CH_2\text{---}CO \end{matrix}\!\!>\!NH$, is obtained; it crystallises in lustrous needles melting at 109—110°, and is not decomposed by hydrochloric acid or potash. Since the phenyldimethylpyrazolidone of the constitution $\begin{matrix} CMe_2\cdot NH \\ | \\ CH_2\text{---}CO \end{matrix}\!\!>\!NPh$, prepared by Prentice, differs from the author's compound, the latter must have the composition assigned above; it follows that the chlorisovaleric acid now described contains the chlorine in the β-position. W. J. P.

Derivatives of Behenic Acid. By GIULIO FILETI (*Gazzetta*, 1897, **27**, ii, 298—302).—The author has prepared behenic acid by

M. Fileti and Ponzio's method (*Gazzetta*, 1893, **23**, ii, 392) of treating erucic acid with moist phosphorus tri-iodide. When treated with bromine and red phosphorus by Volhard's method, it yields *a-bromobehenic acid*, $C_{22}H_{43}BrO_2$, which melts at 70°, and is soluble in the ordinary organic solvents; its *ethylic* salt, $C_{24}H_{47}BrO_2$, is crystalline and melts at 49—51°.

a-Hydroxybehenic acid, $C_{22}H_{44}O_3$, is obtained by heating a-bromobehenic acid with concentrated aqueous potash at 130° in a reflux apparatus, pouring into water, and precipitating with sulphuric acid; it melts at 96—97°, is very soluble in the ordinary organic solvents, and yields an *ethylic* salt melting at 70—71°. If alcoholic potash is used in preparing the hydroxy-acid, a small yield is obtained, most of the product being converted into *a-ethoxybehenic acid* which melts at 60°.

a-Cyanobehenic acid, $C_{23}H_{43}O_2N$, is prepared by heating the bromo-acid in alcoholic solution with potassium cyanide and decomposing the product with hydrochloric acid; it crystallises in white needles, melts at 87—89° and decomposes at 180°, probably yielding the nitrite. When boiled with alcoholic soda, it yields *eicosylmalonic acid*, $C_{23}H_{43}O_4$, which crystallises in needles, melts at 119—120°, and gives off carbonic anhydride at 150°, probably yielding behenic acid.

W. J. P.

Active Constituent of Castor Oil. By HANS MEYER (*Chem. Centr.*, 1897, i, 662; from *Arch. expt. Path. Pharm.*, **38**, 336—345. Compare Abstr., 1897, i, 591—592).—The purgative action of castor oil is not affected by heating the oil to 300°, or by the action of dry hydrogen chloride. Ricinoleic acid, which is, as Buchheim observed, just as effective as castor oil, does not lose this property by heating to 300°, or by boiling with potassium hydroxide solution, but it is converted by the action of mineral acids into ψ-ricinoleic acid, whose alkylic salts are inactive. Ricinolamide is inactive, but yields an active ricinoleic acid. Castor oil owes its purgative property to the presence of ricinoleic acid, or such compounds of it as are decomposed into ricinoleic acid in the intestines: thus magnesium ricinoleate which is not decomposed is inactive. *Barium* ricinoleate, when purified by repeated crystallisation from alcohol, melts at 132°, and contains water which is not expelled at 120°; the cadmium salt is anhydrous. *Ethylic ricinoleate*, prepared by heating sodium ricinoleate with ethylic iodide at 150—170°, is a light brown liquid of sp. gr. = 0·9176 at 20°/24°; *methylic ricinoleate* is prepared in a similar way. *Ethylic ψ-ricinoleate*, which has a sp. gr. = 0·9294 at 20°/24°, is prepared by passing hydrogen chloride into a hot solution of ricinoleic acid in absolute alcohol, treating the product with water and calcium carbonate, and extracting with light petroleum. *Barium ψ-ricinoleate* melts at 117—118°.

E. W. W.

Separation of the Two Desmotropic Forms of Ethylic Acetoacetate. By ROBERT SCHIFF (*Ber.*, 1898, **31**, 205—209).—By the action of benzylideneaniline on ethylic acetoacetate under different conditions, three distinct isomeric additive products have been prepared. When molecular quantities of the two substances are rubbed

together in a dish which is well cooled with water, a thick syrup is obtained, but this soon sets into a hard, white, crystalline mass. After dissolving in benzene and precipitating with light petroleum, small, crystalline aggregates of the compound $C_{19}H_{21}NO_3$ are obtained; its melting point is 93—95°. When the two substances react in the proportion of 1 molecule of benzylidene aniline to 2 of the acetate, the product, after freeing from the excess of acetate and purification as above, melts at 103°. If, however, a few drops (0·2 gram) of piperidine are introduced in the second reaction, a third isomeride, melting at 78°, is obtained. All three substances are optically inactive, and have the same molecular weight.

The author considers that his results support the view that ethylic acetoacetate is a mixture of the "keto" and "enol" forms. The substance melting at 78° is supposed to be the derivative of the "keto" form, and the one melting at 103° is a derivative of the "enol" form. The product, which melts at 95°, is a mixture of the other two, and can readily be obtained synthetically by crystallising a mixture of the two isomerides melting at 78° and 103°. Both the latter compounds can be converted into the mixture melting at 95° by warming with dilute methylic or ethylic alcohol, or by heating for some time at a temperature slightly above their melting points. The two compounds melting at 95° and 103° readily yield deep cherry-red colorations with 35—40 per cent. alcohol and ferric chloride; the compound melting at 78° gives a yellow coloration, which changes to red in the course of a few hours, owing probably to gradual enolisation. Concentrated alcohol causes this change much more rapidly. The enol form (103°) appears to dissolve to a certain extent in alkalis and alkali carbonates. J. J. S.

Formation of Ethereal Salts. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, **18**, 629—657. Compare Abstr., 1895, i, 420; 1896, i, 95; 1897, i, 55; and this vol., i, 30).—The author discusses the results he has hitherto obtained; his views are summarised as follows. (1) When alkylic iodides interact with the acid salts of unsymmetrical dicarboxylic acids, the alkyl radicle becomes attached to the carboxyl group which has the greater electrolytic dissociation constant. (2) A similar law regulates the interaction of alcohols with the anhydrides of unsymmetrical dicarboxylic acids. (3) The formation of ethereal salts by the action of these acids on alcohols in the presence of hydrogen chloride is independent of dissociation constants, and depends solely on the structure of the acid molecule, as pointed out by Victor Meyer. The same law holds for the alkaline hydrolysis of the salts. (4) This similarity between the behaviour of acids with alcohols in presence of hydrogen chloride, and that of the ethereal salts on hydrolysis with alkalis, is best explained by assuming that, in both cases, an intermediate compound is formed by addition to the carboxyl group, as was originally assumed by Henry.

The author divides the methods of formation of ethereal salts into two classes; the first, in which the governing factor is the strength of the carboxyl group, includes the methods based on the interaction of salts of the acid with alkylic iodides, and of alcohols with acid

anhydrides. The interaction of alcohols and acids in presence of hydrogen chloride is a method of the second class, in which the conditioning factor is molecular constitution. A series of experiments are described, showing that the interaction of acid and alcohol in presence of sulphuric acid is also a method of the second class.

In the presence of a small quantity of sulphuric acid, β-monomethylic hemipinate is almost the sole product of the action of methylic alcohol on hemipinic acid; when an excess of sulphuric acid is used, and the mixture cooled, hemipinic anhydride alone is formed, but on heating the mixture, dimethylic hemipinate and traces of the α- and β-monomethylic salts are obtained. Methylic alcohol does not combine with hemipinic acid in presence of methylic potassium sulphate; α-monomethylic hemipinate is formed, however, when the acid and alcohol are heated alone in a sealed tube at 100°; this is probably due to the intermediate formation of hemipinic anhydride (compare this vol., i, 30). Symmetrical tribromobenzoic acid is not acted on when heated with methylic alcohol at 100°, or when the mixture is boiled with a small quantity of sulphuric acid; if, however, an excess of this acid is used, a 12 per cent. yield of the methylic salt is obtained.

W. A. D.

Preparation of Pure Oxalic Acid. By RUDOLF RIECHELMANN (*Chem. Centr.*, 1897, i, 539; from *Zeit. f. öffentl. Chem.*, **3**, 13).—Pure oxalic acid is obtained from the commercial acid by crystallising once from ether, and then once from water. Comparatively large quantities of the acid may be conveniently dissolved in ether by using a Soxhlet's extractor fitted with a Schleicher and Schüll's cartridge.

E. W. W.

Zirconium Oxalates. By FRANCIS P. VENABLE and CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1897, **19**, 12—18).—On adding a saturated solution of oxalic acid to a slightly acid solution of zirconium chloride, a gelatinous precipitate, of the composition $Zr(C_2O_4)_2,2Zr(OH)_4$ is produced, and the filtrate after a time yields another precipitate, $2Zr(C_2O_4)_2,3Zr(OH)_4$; these basic oxalates are soluble in acids with difficulty, and are in an extremely fine state of division, passing through the best filter paper. As all the oxalates and double oxalates examined lose oxalic acid when heated at 100°, they had to be dried between filter paper.

When zirconium hydroxide dissolved in excess of a solution of oxalic acid is evaporated, a *salt* of the composition $Zr(C_2O_4)_2,H_2C_2O_4 + 8H_2O$ is produced, and not the normal oxalate. Zirconium oxalate shows no decided tendency to form definite combinations with the alkali oxalates, but rather a power to crystallise with them in any proportions.

When a solution of zirconium hydroxide in oxalic acid is nearly neutralised with sodium hydroxide and evaporated, small, hard, prismatic crystals are obtained, probably of the composition $Zr(C_2O_4)_2,3Na_2C_2O_4,H_2C_2O_4 + 5H_2O$. Under similar conditions, potassium and ammonium hydroxides yield respectively the *salts* $2Zr(C_2O_4)_2,2K_2C_2O_4,H_2C_2O_4 + 8H_2O$ and $Zr(C_2O_4)_2,2(NH_4)_2C_2O_4$; the latter could not be recrystallised without change.

A. W. C.

Action of Dimethylamine on Diethylic Fumarate and Maleate. By WILHELM KÖRNER and ANGELO MENOZZI (*Real. Accad. Linc.*, 1896, [v], **5**, i, 456—459).—On heating diethylic fumarate with an alcoholic solution of dimethylamine for 3 days in a closed tube at 105—110°, distilling the product from a water bath, and adding ether to the residue, tetramethylasparagine is deposited whilst diethylic dimethylaspartate remains dissolved in the ether.

Tetramethylasparagine, $NMe_2 \cdot CH(NMe_2) \cdot CH_2 \cdot COOH$, crystallises in colourless needles melting at about 104°, and is very soluble in alcohol; when heated with barium hydroxide, it yields dimethylamine and dimethylaspartic acid, together with fumaric acid resulting from the decomposition of the latter.

Diethylic dimethylaspartate, $C_{10}H_{19}NO_4$, is a highly refractive liquid which has a slight odour and is very sparingly soluble in water; it has the sp. gravities = 1·0418, 1·0306, and 0·9702 at 0°, 15°, and 50° respectively, referred to water at 0°. When heated with barium hydroxide solution in a closed tube, it yields *barium dimethylaspartate* crystallising in needles; the acid itself, $C_6H_{11}NO_4$, crystallises in large, colourless, monosymmetric prisms melting at 185°; $a:b:c = 1·2141:1:0·6340$; $\beta = 78° 19'$. The diethylic salt gives a quantitative yield of diethylic fumarate when boiled with sulphuric acid.

On heating diethylic maleate with dimethylamine solution, the same products are obtained as with the fumarate. W. J. P.

Homologues of Ethylic Oxalacetate. By WILHELM WISLICENUS and MAX KIESEWETTER (*Ber.*, 1898, **31**, 194—200).—Ethylic oxalobutyrate, like the coresponding oxalopropionate, readily decomposes when heated, ethylic ethylmalonate being formed and carbonic oxide evolved; the homologues, however, behave towards ammonia in a different manner from ethylic oxalate itself, as an amidoimide is formed, and not an additive compound. This amido-imide is analogous in constitution to the substance obtained by the action of aniline on ethylic oxalopropionate (Wislicenus and Spiro, Abstr., 1890, 378).

Amidocitraconimide, $NH<\begin{matrix} CO \cdot C \cdot NH_2 \\ \quad\; \| \\ CO \cdot CMe \end{matrix}$, obtained by the action of ammonia on ethylic oxalopropionate, forms yellow crystals, melts at 230°, and is decomposed by boiling aqueous soda, with evolution of ammonia and formation of sodium oxalate; ethylic oxalobutyrate yields a similar compound, which also forms yellow crystals, melts at 204°, and is probably *amidoethylmaleinimide*, $NH<\begin{matrix} CO \cdot C \cdot NH_2 \\ \quad\; \| \\ CO \cdot CEt \end{matrix}$.

Ethylic oxalopropionate reacts with benzaldehyde in a similar manner to ethylic oxalacetate, *ethylic ketophenylhomoparaconate*, $O<\begin{matrix} CO \text{——} CO \\ \qquad\quad | \\ CHPh \cdot CMe \cdot COOEt \end{matrix}$, being formed; this, which is an oil, has not yet been obtained pure. It is decomposed by boiling dilute sulphuric acid, yielding benzaldehyde, carbonic anhydride, alcohol, and propionylformic acid, its constitution being thus proved.

Ethylic oxalisobutyrate (ethylic dimethyloxalacetate),

$$COOEt \cdot CO \cdot CMe_2 \cdot COOEt,$$

is formed in very small amount when ethylic sodio-oxalopropionate is treated with methylic iodide, but has only been obtained as a slightly impure oil boiling between 225 and 230° without any evolution of carbonic oxide. When heated with alcoholic soda, it yields oxalic and isobutyric acids, so that no doubt exists as to its constitution. Ammonia decomposes it with formation of oxamide and isobutyramide, whilst aniline yields oxanilide, and with phenylhydrazine it forms a *hydrazone*, $COOEt\cdot C(N_2HPh)\cdot CMe_2\cdot COOEt$, which melts at 90—91° and cannot be made to yield a pyrazolone. A. H.

Action of Cyanogen on Ethylic Sodiomalonate. By WILHELM TRAUBE (*Ber.*, 1898, **31**, 191—193).—Ethylic sodiomalonate absorbs cyanogen with development of heat, a red, crystalline compound being formed which most probably has the constitution $\begin{matrix} NH{:}C\cdot CNa(COOEt)_2 \\ | \\ NH{:}C\cdot CNa(COOEt)_2 \end{matrix}$; water converts this into a substance of the formula $C_{12}H_{14}O_8N_2Na_2$, which crystallises in brownish needles, is sparingly soluble in water, and on treatment with hydrochloric acid yields a yellowish substance, $C_{12}H_{12}O_6N_2$, which may also be obtained by the direct action of hydrochloric acid on the red compound. The free acid, corresponding with the red salt, is formed when the latter is warmed with aqueous soda and then acidified; it crystallises in pale yellow needles, is decomposed by boiling water, and with phenylhydrazine acetate yields a brown, crystalline *derivative* melting at 210°.

When the red sodium salt is treated with methylic iodide, a derivative, $C_{14}H_{16}O_6N_2$, is formed which crystallises in deep yellow needles and melts at 150°. Similar compounds are formed by the action of cyanogen on ethylic sodioacetoacetate and other analogous compounds.

A. H.

Copper Derivatives of Ethylic Dicarboxyglutaconate. By WILHELM WISLICENUS (*Ber.*, 1898, **31**, 140—142).—Ethylic dicarboxyglutaconate yields two copper derivatives, *normal*, $(C_{15}H_{21}O_8)_2Cu$, and *basic*, $C_{15}H_{21}O_8\cdot Cu\cdot OH$. The normal compound is readily obtained when a 15 per cent. alcoholic solution of the ethylic salt is treated with the requisite quantity of copper acetate dissolved in 15—20 times its weight of water. It crystallises from alcohol in small, yellowish-green needles melting at 175—176°, and its alcoholic solution gives a deep violet coloration with ferric chloride.

The basic derivative is obtained together with the normal one when warm alcoholic solutions of the ethylic salt and copper acetate are used, or, still better, when an aqueous solution of the sodium derivative of the ethylic salt is precipitated with an excess of copper acetate solution. It can be separated from the normal derivative by the aid of methylic alcohol, in which it is only sparingly soluble. Recrystallised from a large quantity of hot methylic alcohol, it is obtained in bluish-green prisms melting at 193—195°. It also gives a violet coloration with ferric chloride.

As it is probable that in all stable metallic derivatives the metal is directly combined with oxygen, the following constitution is given to the metallic derivative of ethylic dicarboxyglutaconate,

$$C(COOEt)_2{:}CH\cdot C(COOEt){:}C(OEt)\cdot OM'.$$

It is thought probable that the ethylic salt, like ethylic acetoacetate, consists of a mixture of a small quantity of the "enol" and much of the "keto" forms, and that by the action of alkalis, ferric chloride, copper acetate, &c., it is rapidly converted into metallic derivatives of the "enol" type. J. J. S.

Syntheses with Ethylic Chlorofumarate. By WALTER BECKH (*Ber.*, 1898, **31**, 47—51).—When ethylic ethane-$\alpha\alpha\alpha_1$-tricarboxylate is mixed with sodium ethoxide in cooled alcoholic solution, ethylic chlorofumarate added, and the mixture finally warmed for an hour on the water bath, *ethylic butylenepentacarboxylate*,

$$COOEt\cdot CH_2\cdot C(COOEt)_2\cdot C(COOEt):CH\cdot COOEt,$$

is formed, and separates as an oil when the alcohol is distilled off and the residue poured into water. It boils at 229—231° under 13 mm. pressure; it is hydrolysed by boiling with baryta water, and the free *acid*, which is very soluble in water, can be obtained crystalline and melts at 173—176°.

A second product is formed in addition, but this is more conveniently obtained by mixing ethylic butylenepentacarboxylate (1 mol.) with sodium (1 atom) and a few drops of absolute alcohol, and heating at 120°. The product, when dissolved in water and acidified, yields an oil which does not boil without some decomposition, even under diminished pressure; it has marked acid properties, and gives a claret coloration with ferric chloride, very possibly it is a ketopentene derivative,

$$\begin{matrix} CH : C(COOEt) \\ | \\ CO\cdot CH(COOEt) \end{matrix} > C(COOEt)_2.$$

Ethylic amylenepentacarboxylate,

$$COOEt\cdot CH_2\cdot CH_2\cdot C(COOEt)_2\cdot C(COOEt):CH\cdot COOEt,$$

was prepared from ethylic carboxyglutarate (propane-$\alpha\alpha\alpha_1$-tricarboxylate) (Emery, Abstr., 1891, 547; in its formation, for ethylic β-bromopropionate the analogous iodo-compound is substituted with advantage) and ethylic chlorofumarate; it boils at 240—250° under 15 mm. pressure. It also condenses with sodium ethoxide at 120°; the product is a syrup, and possibly has the constitution

$$CO < \begin{matrix} CH{=\!=}C(COOEt) \\ CH(COOEt)\cdot CH_2 \end{matrix} > C(COOEt)_2.$$

C. F. B.

Molecular Weight of Lactimide. By GEORGE M. RICHARDSON and MAXWELL ADAMS (*Amer. Chem. J.*, 1898, **20**, 129—133).—By determining its molecular weight by the cryoscopic method, using acetic acid as solvent, the authors confirm the structural formula, $CHMe < \begin{matrix} NH\cdot CO \\ CO\cdot NH \end{matrix} > CHMe$ for lactimide. W. A. D.

Stability of Imides of Dibasic Acids. By ARTURO MIOLATI (*Real. Accad. Linc.*, 1896, [v], **5**, ii, 375—380).—In continuation of his previous work (Abstr., 1896, ii, 242), the author has made further determinations of the velocity of hydrolysis of the imides of dibasic acids; the velocity constants *Ac* are given in the accompanying table.

No determinations were possible with orthobenzoicsulphinide, the

Substance.	$A\,c$	Substance.	$A\,c$
Citraconic imide	1·2139	Quinolinic imide	0·2561
Pyrocinchonic imide	0·3184	Cinchomeric imide	0·3977
Phthalimide	0·08705		

aqueous solution being acid, and immediately becoming neutral on adding 1 molecular proportion of soda. W. J. P.

Biuret Reactions. By Hugo Schiff (*Annalen*, 1897, **299**, 236—266. Compare Abstr., 1896, i, 284 and 635).—The author describes in detail the results already published. The derivatives of biuret, malonamide, and oxamide which give the biuret reaction are distinguished from those which do not. M. O. F.

Thiocarbamide Derivatives. By Rudolf Andreasch (*Ber.*, 1898, **31**, 137—138).—Thiohydantoins were obtained by treating the different thiocarbamides with ethylic chloracetate or α-bromopropionate in alcoholic solution, and after precipitation with ammonia were extracted with ether.

Hantzsch's system of nomenclature is adopted.

$$\left.\begin{array}{l}(\beta)CH_2—S \\ (\alpha)\overset{|}{C}O\cdot NH_{(\nu)}\end{array}\right> C{:}NH\ (n).$$

n-*Ethylthiohydantoin*, $C_5H_8N_2SO$, forms colourless needles melting at 144°. n-ν-*Diethylthiohydantoin* forms colourless needles, is very readily soluble, and melts at 41°; β-*Methyl*-n-*ethylthiohydantoin*, *ethylallylhydantoin*, and *ethylphenylhydantoin* were obtained in the form of yellowish, syrupy oils.

Phenyl-β-benzylidenethylthiohydantoin, $C_{18}H_{16}N_2SO$, obtained by the action of benzaldehyde on ethylphenylhydantoin, melts at 90°. *Phenyl-β-methylethylthiohydantoin* melts at 101°.

Thioparabanic acids were obtained by passing cyanogen gas into the alcoholic solutions of the thiocarbamides and then heating the resulting cyanides with hydrochloric acid; they were mostly purified by extraction with ether, and when heated with silver nitrate in alcoholic solution gave the corresponding parabanic acids.

Ethylthioparabanic acid forms golden-yellow needles melting at 66°. *Ethylparabanic acid* crystallises in colourless needles melting at 45°. *Diethylthioparabanic acid* forms flat, yellow needles or thick prisms melting at 102°. *Diethylparabanic acid*, colourless needles melting at 46°. *Methylethylthioparabanic acid*, slender, yellow needles melting at 62°. *Methylallylthioparabanic acid* melts at 56° and *methylallylparabanic acid* at 42—43°. *Ethylallylthioparabanic* acid melts at 54°, and *ethylallylparabanic acid* at 66°. *Phenylmethylthioparabanic acid*, which melts at 170° and crystallises in sulphur-yellow needles or orange-yellow, six-sided plates, is decomposed by barium carbonate, yielding oxalic acid and phenylmethylthiocarbamide. *Phenylmethylparabanic acid* melts at 148°, *phenylethylthioparabanic acid*, which, in appearance, resembles lead iodide, melts at 174° and *phenylethylparabanic acid* at 97°. *Diphenyl-*

thioparabanic acid crystallises in bronze-coloured, woolly needles melting at 228°. *Diparatolylthioparabanic acid* melts at 236°.

Unsymmetrical disubstituted thiocarbamides do not combine with cyanogen. J. J. S.

α-Methyladipic Anhydride and 2-Methylketopentamethylene. By CLEMENTE MONTEMARTINI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 228—231. Compare Abstr., 1897, i, 19).—On distilling α-methyladipic acid with acetic chloride under reduced pressure, it is converted into a very unstable *anhydride*, $\begin{matrix}CH_2\cdot CHMe\cdot CO \\ | \\ CH_2\cdot CH_2—CO\end{matrix}\!\!>\!O$, which, by distillation, is partially converted into a ketopentamethylene,

$$\begin{matrix}CH_2\cdot CH_2 \\ | \\ CH_2—CO\end{matrix}\!\!>\!CHMe,$$

with loss of carbonic anhydride.

2-*Methylketopentamethylene*, which is best prepared by distilling α-methyladipic acid with lime and iron filings, boils at 142—144°, has a mint-like odour and is lighter than water. Its *semicarbazone*, $C_7H_{13}N_3O$, forms minute crystals melting at 171°. W. J. P.

Iodine Derivatives of Monochlorobenzene. By CONSTANTIN I. ISTRATI (*Chem. Centr.*, 1897, i, 1161; from *Bull. Soc. Sciinte*, 6, 47—55).—When a mixture of 250 grams of monochlorobenzene with 500 grams of iodine and 350 c.c. of sulphuric acid is boiled for 38 hours, the product consists of two distinct layers of liquid. By shaking the whole with water, it forms a rather viscous liquid which deposits a coarsely crystalline mass and a brownish-red precipitate of francein. The decanted liquid is neutralised with calcium and barium carbonates, the excess of iodine and the francein are removed by concentrated potassium hydroxide solution, and the residual liquid then thoroughly washed with boiling water; when this liquid is distilled under 60 mm. pressure, a liquid and a solid substance come over at 200—280°. The latter is also left behind when the distillation is continued under atmospheric pressure from 135—310°, or by distilling to 270° in a vacuum. By repeatedly crystallising from chloroform, it yields *chlorotri-iodobenzene*, $C_6H_2ClI_3$ [$Cl : I_3 = 1 : 2 : 4 : 6$], melting at 162—164°.

The liquid portion of the distillate, when fractionated, yields chlorobenzene, large, colourless, transparent crystals of iodobenzene, and finally *chlorodi-iodobenzene*, $C_6H_3ClI_2$ [$Cl : I_2 = 1 : 2 : 4$], a colourless liquid which gradually becomes faintly red, boils at 221° under 78 mm. pressure, remains liquid at $-12°$, is soluble in alcohol and chloroform, and has a remarkably high sp. gr. = 2·5547—2·5552 at 0°, and 2·5197—2·5201 at 25°. When treated with fuming nitric acid at 80°, di-iodochlorobenzene yields *di-iodochloronitrobenzene*,

$$C_6H_2ClI_2\cdot NO_2\ [Cl : I_2 : NO_2 = 1 : 2 : 4 : ?],$$

an extremely volatile substance which crystallises from alcohol and melts at 94—95°. E. W. W.

The Explosive Decomposition of Nitro-compounds when Mixed with Substances Rich in Oxygen. By CHRISTIAN GÖTTIG (*Ber.*, 1898, 31, 25—28).—The powder examined contained in 100 parts:

barium nitrate, 9·83; nitrotoluenes (mixture of 2 : 4 : 6-trinitrotoluene with 2-nitrotoluene), 22·22; nitrocelluloses, 67·96; the percentage of nitrogen, estimated by the Dumas method, was 12·33. Some of the powder was exploded in a small chamber by means of a platinum wire heated electrically. The solid residue formed 14·28 per cent. of the whole, and contained, in 100 parts, organic matter (carbon), 9·51; barium carbonate, 64·44; residue insoluble in acids, with some alkali carbonates, iron compounds, &c., 26·05. The water formed amounted to 8·64 per cent. of the powder. The (dry) gases formed in the explosion contained, in 100 vols.: nitric oxide, 10·75; carbonic anhydride, 27·48; carbonic oxide, 36·02; methane, 9·01; hydrogen, 1·94; nitrogen, 14·80. The following equation is given as representing the decomposition, $11C_{12}H_{14}(NO_3)_6O_4 + 10C_6H_2Me(NO_2)_3 + 4Ba(NO_3)_2 = 4BaCO_3 + 49H_2O + 9C + 93CO + 72CO_2 + 28NO + 5H_2 + 24CH_4 + 38N_2$.

C. F. B.

Composition of Wool Fat. V. By L. Darmstaedter and Isaac Lifschütz (*Ber.*, 1898, **31**, 97—103. Compare Abstr., 1896, i, 522; 1897, i, 180).—The soft fat, left after the removal of the wool wax, as already described, amounts to about 85—90 per cent. of the whole, and yields on hydrolysis about 40—45 per cent. of acids; these, which consist chiefly of an oily acid of unknown constitution, myristic acid, and carnaubaic acid, will be more particularly described in a further communication.

The alcohols obtained from the soft fat do not appear to contain any cholesterol, but can be divided into nearly equal fractions, one of which is insoluble in cold methylic alcohol, whilst the other is readily soluble. The former of these agrees in most of its properties with Schulze's isocholesterol (this Journal, 1873, 920), but appears to differ from it in crystalline form, solubility, and composition. It is insoluble in water and methylic alcohol, but readily soluble in most other solvents, and crystallises in short, thick, microscopic prisms, which melt at 137—138° when dry. The air-dried substance loses 2·7 per cent. of water at 80°, leaving a residue which has the composition $(C_{26}H_{45}O)_2O$. When a drop of sulphuric acid is added to its solution in acetic acid, a yellow solution with a green fluorescence is produced, showing a characteristic absorption band between the lines D and E of the solar spectrum.

The second fraction consists of a thick, honey-like mass, which will be described in a further communication.

The examination of the alcohols obtained from the wool wax has shown that a small amount of cerylic alcohol is present. Among the acids obtained from the same substance, a small amount of a compound has been isolated, which agrees in nearly all its properties with cerotic acid, but appears to differ from the latter in its behaviour towards solvents and in the fact that its magnesium salt melts at 174—176°, whereas magnesium cerotate is stated to have the melting point 140—145°.

A. H.

The Glycol obtained from Isobutaldehyde and Benzaldehyde and its Behaviour with Sulphuric Acid. By Richard Reik (*Monatsh.*, 1897, **18**, 598—612).—The author finds that the glycol

obtained by the condensation of isobutaldehyde with benzaldehyde (Fossek and Swobada, Abstr., 1891, 31), is a 3-phenyl-2 : 2-dimethylpropane-1 : 3-diol, $OH\cdot CH_2\cdot CMe_2\cdot CHPh\cdot OH$, as, on oxidising it with cold potassium permanganate solution, benzoic and acetic acids were obtained, together with phenylisopropyl ketone, which was characterised by its oxime.

On heating 3-phenyl-2 : 2-dimethylpropane-1 : 3-diol with 14 per cent. sulphuric acid, β-butenylbenzene (3-phenyl-2-methylpropene-2), $CMe_2{:}CHPh$ (Perkin, Trans., 1879, 136), is formed, along with a *methylene ether* of the glycol, $CMe_2<\begin{matrix}CH_2\text{—}O\\CHPh\cdot O\end{matrix}>CH_2$. This substance can also be prepared by the condensation of formaldehyde with the glycol, using Tollens' method; it is a white, crystalline substance which melts at 39°, and boils at 135° under 15 mm. pressure. The decomposition of the glycol is explained by Lieben in the following equations, it being assumed that formaldehyde is liberated in the first instance.

i. $OH\cdot CHPh\cdot CMe_2\cdot CH_2\cdot OH + H_2O = OH\cdot CHPh\cdot CHMe_2 + CH_2(OH)_2$
ii. $OH\cdot CHPh\cdot CHMe_2 = CHPh{:}CMe_2 + H_2O$
iii. $CH_2(OH)_2 + \begin{matrix}OH\cdot CH_2\\OH\cdot CHPh\end{matrix}>CMe_2 = CH_2<\begin{matrix}O\text{—}CH_2\\O\cdot CHPh\end{matrix}>CMe_2 + 2H_2O$

W. A. D.

Final Product of the Action of Nitrogen Chloride on Dimethylaniline. By W. HENTSCHEL (*Ber.*, 1898, 31, 246—249. Compare this vol., i, 130).—The product obtained by the action of nitrogen chloride on a benzene solution of dimethylaniline is shown to be $C_{24}H_{13}Cl_{19}N_2$, probably $C_6H_6Cl_5\cdot N(C_6HCl_4)\cdot N(C_6HCl_4)\cdot C_6H_5Cl_6$. It is best to saturate the solution first with hydrogen chloride, then with chlorine, and finally to add an excess of nitrogen chloride and to leave the mixture for several hours in the dark. An alcoholic solution of sodium ethoxide (12 atoms of sodium to 1 mol. of the compound) readily reacts with the product, yielding 2 : 3 : 4 : 6-tetrachloraniline and chlorinated phenols. Boiling alcohol also decomposes the compound, yielding methylamine hydrochloride and symmetrical trichlorophenol, together with other substances. Zinc dust and acetic acid react with the compound, yielding trichlormethylaniline. J. J. S.

Action of Trimethylamine, Dimethylamine, and Methylamine on Bromacetophenone. By HANS RUMPEL (*Chem. Centr.*, 1897, i, 494—495; from *Diss. Marburg*, 1897).—According to the author, bromacetophenone is best prepared by the action of bromine on acetophenone in aqueous solution. By the action of trimethylamine on this compound, *phenacyltrimethylammonium bromide*, $NMe_3Br\cdot CH_2Bz$, is formed; it melts at 207°, is easily soluble in alcohol and in water, but almost insoluble in ether. The aurochloride crystallises in characteristic dark-brown leaflets of variable composition. The oxime is very soluble in water and alcohol, but insoluble in ether and light petroleum. By the action of sodium amalgam on the bromide, hydrogen bromide, trimethylamine, and an oily substance, which is perhaps phenylmethylcarbinol, are formed. Neither fuming hydrochloric acid nor sodium carbonate has any action on the bromide at 150°, but sodium hydroxide decomposes it into trimethylamine and benzoic acid.

The corresponding *chloride*, obtained by the action of silver chloride

on the bromide, melts at 202°; the *aurochloride* at 180—181°, the *platinochloride* at 235—240°, the *mercurochloride* at 205°, and the copper double salt at 200—201°. The *oxime* obtained from the chloride melts at 186°, and forms an *aurochloride* and a *platinochloride* which melt at 147—148° and 199—201° respectively, and cannot be recrystallised owing to decomposition. The oxime is not attacked by acetic chloride or acetic anhydride, but is decomposed by 25 per cent. hydrochloric acid or by concentrated sulphuric acid, with formation of hydroxylamine and the corresponding salt of phenacyltrimethylammonium. On reduction with sodium amalgam, the oxime yields trimethylamine and α-phenylethylamine. Phosphorus pentachloride brings about a molecular rearrangement, forming $NMe_3Cl{\cdot}CH_2{\cdot}CO{\cdot}NHPh$; the *platinochloride* of this compound decomposes at 210—215°, and the *aurochloride* melts at 174—175°; both these salts are more stable than the oxime itself.

By the action of dimethylamine on bromacetophenone, *phenacyldimethylamine hydrobromide*, $NMe_2{\cdot}CH_2{\cdot}COPh,HBr$, and *diphenacyldimethylammonium bromide*, $NMe_2Br(CH_2Bz)_2$, are formed; the former crystallises in nodules, melts at 184—186°, is very easily soluble in cold water, and yields a platinochloride melting at 206° and an aurochloride melting at 158°, whilst the latter crystallises in needles, is slightly soluble in cold water, melts at 156°, and forms a *platinochloride* and an *aurochloride* which melt at 201—202° and 112—114° respectively.

By the action of methylamine on bromacetophone, *phenacylmethylamine hydrobromide*, $NHMe{\cdot}CH_2{\cdot}COPh,HBr$, and *diphenacylmethylamine hydrobromide*, $NMe(CH_2Bz)_2,HBr$, are formed; the former crystallises in leaflets, is easily soluble in cold water, melts at 203°, and forms an *aurochloride* melting at 134° and a *platinochloride* melting at 200°. The latter crystallises in needles, is slightly soluble in cold water, and melts at 229—230°. Its *aurochloride* melts at 240° and the *platinochloride* at a higher temperature. Strychnine acetophenone bromide (Abstr., 1897, i, 644—645) decomposes at 160°; the *aurochloride* of the corresponding chloride melts at 190—193°, and the *platinochloride* at 220—222°. E. W. W.

The so-called Nitramines and Isonitramines and their Ethers. By ARTHUR R. HANTZSCH (*Ber.*, 1898, 31, 177—187).—The nitramines yield two isomeric methylic ethers, in one of which the alkyl group is combined with nitrogen and in the other with oxygen. The isonitramines, in a similar manner, yield two isomeric ethers, but both of these are oxygen ethers, one being derived from nitrosohydroxylamine, whilst the constitution of the second is unknown.

Nitramine, $R{\cdot}NH{\cdot}NO_2$; nitrogen ether, $R{\cdot}NMe{\cdot}NO_2$; oxygen ether of unknown constitution, $R{\cdot}N_2O{\cdot}OMe$.

Isonitramine, $R{\cdot}N(OH){\cdot}NO$; nitrosohydroxylamine ether, $R{\cdot}N(OMe){\cdot}NO$; oxygen ether of unknown constitution, $R{\cdot}N_2O{\cdot}OMe$.

In endeavouring to prepare all the four isomeric derivatives corresponding with phenylnitramine and isonitramine, the author found that only the already known ether of the isonitramine could be obtained, but he succeeded in preparing four methyl ethers derived from paranitrobenzylnitramine and the corresponding isonitramine.

Benzylurethane (ethylic benzylcarbamate) has already been

described by Cannizzaro, who, however, gives the melting point as 86°, whilst the author finds it to be 48—49°. It was found impossible to prepare benzylnitro-urethane from this compound, whereas *paranitrobenzylurethane*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot COOEt$, can readily be obtained from it and melts at 118°. *Paranitrobenzylnitrourethane*,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(NO_2) \cdot COOEt,$$

is formed by the action of pure nitric acid on benzylurethane and yields *paranitrobenzylnitramine*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N_2O_2H$, on treating it with ammonia in ethereal solution and acidifying; this nitramine melts at 116° and yields white, crystalline salts with dilute alkalis, which yield the original nitramine when acidified. When the sodium salt is treated with methylic iodide, nitrobenzylmethylnitramine,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NMe \cdot NO_2,$$

the nitrogen ether is formed and is identical with the product melting at 72° obtained by Franchimont (*Rec. trav. chim.*, 14, 246), from methylnitramine and paranitrobenzylic chloride. The isomeric *oxygen ether,* obtained by the action of methylic iodide on the silver salt, crystallises in long needles melting at 115—116° and when heated with alcoholic hydrogen chloride passes into the nitrogen ether melting at 72°.

Nitrobenzylisonitramine, when etherified by the action of methylic iodide on its silver salt, yields two isomeric ethers; that formed in smaller quantity is *nitrobenzylnitrosohydroxylamine methyl ether*,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot N(OMe) \cdot NO,$$

which melts at 26°, gives Liebermann's reaction with phenol and sulphuric acid, and is identical with the product obtained from α-methylhydroxylamine and paranitrobenzylic iodide. The *isomeride*, however, which is the chief product, is still of unknown constitution, and crystallises in well-developed needles melting at 145—146°. Nitrobenzylnitramine, the corresponding isonitramine, and the two isomeric oxygen ethers of uncertain constitution are all decomposed by concentrated sulphuric acid with formation of paranitrobenzylic alcohol and its sulphonic acid. The oxygen ether of nitrobenzylnitramine is decomposed in the cold by alcoholic potash, nitrous oxide being evolved and nitrobenzylic alcohol produced, whilst the isonitramine derivative simply yields a deep violet-coloured solution, which changes colour when heated but has not yielded any definite products of decomposition.

An unsuccessful attempt was also made to ascertain the probable formulæ of the two oxygen ethers of uncertain constitution by a study of their physical properties; it was, however, found that, whilst they have identical molecular refractions, the nitramine derivative has a somewhat greater molecular volume in solution than the isonitramine compound. The unetherified nitramine and isonitramine, on the other hand, have identical molecular volumes in solution. No adequate explanation of the isomerism of these two oxygen ethers has therefore yet been found. A. H.

Action of Phosgene and of Ethylic Chloroformate on Paracetamidophenols and on Parahydroxyphenylurethanes. By C. EMANUEL MERCK (*Chem. Centr.*, 1897, i, 468—469; from *Ber. ü. d. Jahr.*, 1896, 5—11).—By the action of phosgene gas and of ethylic

chloroformate respectively on paracetamidophenol, *paradiacetanilide carbonate*, $(NHAc\cdot C_6H_4\cdot O)_2CO$, and *ethylic paracetanilide carbonate*, $NHAc\cdot C_6H_4\cdot O\cdot COOEt$, are formed; the former crystallises in leaflets, melts at about 200°, and is slightly soluble in water and easily in alcohol, the latter crystallises from alcohol in needles, melts at 120° and is very slightly soluble in water. Parahydroxyphenylurethanes undergo similar reactions with phosgene and ethylic chloroformate. By means of these reactions, the author has prepared the following compounds, parapropionanilide carbonate, $CO(O\cdot C_6H_4\cdot NH\cdot C_3H_5O)_2$, crystallises from alcohol, melts at 180°, and is slightly soluble in water; parabenzoylanilide carbonate, $CO(O\cdot C_6H_4\cdot NHBz)_2$, a fine, crystalline powder, melts and decomposes at 220°; it is slightly soluble in ether, almost insoluble in alcohol and in water; paraphenylethylurethane carbonate, $CO(O\cdot C_6H_4\cdot NH\cdot COOEt)_2$, forms white leaflets, melts at 184°, and is easily soluble in alcohol, very slightly in water; paraphenylpropylurethane carbonate, $CO(O\cdot C_6H_4\cdot NH\cdot COOPr)_2$, forms white leaflets, melts at 155°, and is slightly soluble in water, easily in ether; propylic paracetanilide carbonate, melts at 105—108°, and is very slightly soluble in water; butylic paracetanilide carbonate forms lustrous crystals and melts at 117—120°; ethylic parapropionanilide carbonate, $COEt\cdot NH\cdot C_6H_4\cdot O\cdot COOEt$, forms needles or plates, melts at 101—103°, and is slightly soluble in water; ethylic parabenzanilide carbonate, $NHBz\cdot C_6H_4\cdot O\cdot COOEt$, crystallises in needles, melts at 183—184°, and is slightly soluble in alcohol, but insoluble in water; phenylglycolylparamidophenylic methylic carbonate or methylic amygdalylanilide carbonate,

$$OH\cdot CHPh\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot COOMe,$$

melts at 135—136°, is very slightly soluble in water, easily in alcohol; phenylglycolylparamidophenylic ethylic carbonate or ethylic amygdalylanilide carbonate, known in commerce as amygdophenin, melts at 162—163°; ethylic paraphenylethylurethane carbonate,

$$COOEt\cdot NH\cdot C_6H_4\cdot O\cdot COOEt,$$

forms lustrous needles, melts at 104—105°, and is very slightly soluble in water, easily in alcohol; ethylic paraphenylpropylurethane carbonate, $COOPr\cdot NH\cdot C_6H_4\cdot O\cdot COOEt$, forms white plates, melts at 94—96°, and is very slightly soluble in water; propylic paraphenylethylurethane carbonate, $COOEt\cdot NH\cdot C_6H_4\cdot O\cdot COOPr$, melts at 54—56°, and is slightly soluble in water. E. W. W.

Electro-Chemical Introduction of Hydroxyl Groups into Azobenzene. By JOHANN HEILPERN (*Zeit. Elektrochem.*, 1897, 4, 89—90).—Azobenzene, dissolved in the smallest quantity of concentrated sulphuric acid, is placed in a porous cell containing the anode, the cathode is immersed in a fairly concentrated solution of caustic potash or of potassium chromate surrounding the porous cell, and a current of 3 to 4 ampères passed for 5 hours; the greenish-black precipitate formed is purified by dissolution in caustic soda and precipitation by hydrochloric acid. The tetrahydroxyazobenzene thus obtained is, when dry, a dark green, amorphous mass, soluble in alkalis or concentrated sulphuric acid with a cherry-red colour, and in glacial acetic acid with a yellow colour; water precipitates it from acid solu-

tions as a dark-red precipitate; 5 grams of azobenzene yield 5 grams of the product. The tetracetyl derivative was obtained in the form of reddish-yellow needles, readily soluble in alcohol and ether, and melting at 240—242°. The substance strongly resembles the parazophenolphloroglucinol described by Benedict and Weselsky (*Ber.*, 1879, 12, 227); it dyes wool and silk yellow, the colour being fast to light, soap, and acids. T. E.

Disazo-compounds from Metaphenylenediamine. By KARL EIERMANN (*Ber.*, 1898, 31, 188—191).—The author has synthesised two isomeric disazo-compounds from metaphenylenediamine, and since neither of them is identical with that obtained from Bismarck-brown by Täuber and Walder, it follows that the constitution assigned by these authors to their compound is correct. *Metamidophenylazometamidophenylazo-metaphenylenediamine*,

$$NH_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(NH_2)\cdot N_2\cdot C_6H_3(NH_2)_2,$$

can be obtained by the following series of operations. Monacetylmetaphenylenediamine readily yields a diazo-solution, which reacts with another molecule of the monacetyl derivative to produce an *amidoazo-compound*, $NHAc\cdot C_6H_4\cdot N_2\cdot C_6H_3(NH_2)\cdot NHAc$; this forms golden-yellow, crystalline flakes melting at 229—230°, and when heated with hydrochloric acid yields triamidoazobenzene. This compound is again converted into a diazo-compound, metaphenylenediamine is added, and the diacetyl derivative of the disazo-compound thus formed, when hydrolysed with hydrochloric acid, finally yields the required substance. The disazo-compound prepared in this way separates from benzene, or a mixture of benzene and phenol, in red, lustrous crystals of the formula $3C_{18}H_{18}N_8,2C_6H_6$, and melts, when free from benzene, at 134°. The isomeric *bis-metamidophenylazo-metaphenylenediamine*, $NH_2\cdot C_6H_4\cdot N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_6H_4\cdot NH_2$, is prepared by acting with metaphenylenediamine (1 mol.) on diazotised monacetylmetaphenylenediamine (2 mols.), and heating the product with hydrochloric acid. It separates from benzene or a mixture of benzene and phenol in reddish-yellow crystals of the composition $C_{18}H_{18}N_8 + C_6H_6$, which, when pure, melts at 116—118°. A. H.

Influence of Methoxyl Groups in Diazotising Aromatic Compounds. By PIETRO BIGINELLI (*Gazzetta*, 1897, 27, ii, 347—357). —A *dinitromethoxycoumarin*, $OMe\cdot C_6H(NO_2)_2<\begin{matrix}O-CO\\CH:CH\end{matrix}$, is obtained on dissolving Tiemann's methoxycoumarin in cooled fuming nitric acid and pouring the product on to ice; it crystallises in yellow needles melting at 149—150°. On reduction with iron filings in acetic acid solution, it yields an *amido*-derivative, $OMe\cdot C_6H(NH_2)_2<\begin{matrix}O-CO\\CH:CH\end{matrix}$, which crystallises in needles or scales melting at 227—228°, and is insoluble in dilute hydrochloric acid; when diazotised, it gives a black, infusible *substance* which is not decomposed by long boiling with dilute sulphuric acid. On diazotising Nietzki and Preusser's diacetamidoquinol (Abstr., 1886, 1024; 1887, 574), a similar black, infusible

substance is obtained, so that the peculiar behaviour of the coumarin derivative towards nitrous acid is not due to its containing the coumarin chain.

By varying the conditions under which methoxycoumarin is nitrated, a *mononitromethoxycoumarin*, $C_{10}H_7NO_5$, may be obtained; it crystallises in yellow needles melting at 155—156°. On reduction with iron in acetic acid solution, this yields a *monamidomethoxycoumarin*, $C_{10}H_9NO_3$, crystallising in prisms which exhibit a blue fluorescence and melt at 222—223°; its *acetyl* derivative, $C_{11}H_{12}NO_4$, crystallises in yellow prisms melting first at 207—208°, and after fusion at 211—212°. On diazotising either the base or the acetyl derivative, a red, infusible *substance* difficult to purify is obtained. A small, relatively pure, portion of this contained nitrogen in quantity corresponding with the composition $C_{20}H_{15}NO_7$; it is soluble in dilute soda, and is precipitated by carbonic anhydride, showing that the coumarin linking still persists.

On diazotising the trimethyl ether of monamidopyrogallol, it yields a *substance*, $C_{16}H_{18}O_8$, crystallising in needles and melting at 243—244°; this is probably a quinhydrone of the constitution

$$OH\cdot C{<}{\begin{matrix}C(OMe)\cdot CH\\C(OMe){:}CH\end{matrix}}{>}C\cdot O\cdot O\cdot C{<}{\begin{matrix}CH\cdot C(OMe)\\CH{:}C(OMe)\end{matrix}}{>}C\cdot OH;$$

it is accompanied by a *substance* which probably has the constitution $OMe\cdot C{<}{\begin{matrix}C(OMe)\cdot CH\\C(OMe){:}CH\end{matrix}}{>}C\cdot NH\cdot O\cdot C{<}{\begin{matrix}CH\cdot C(OMe)\\CH{:}C(OMe)\end{matrix}}{>}COMe$ being insoluble in soda, and unaltered by boiling with dilute sulphuric acid.

It is concluded that, in cyclic compounds, the presence of methoxyl groups impedes diazotisation, and that during the diazotisation of such compounds, condensation products are mainly formed.

W. J. P.

Action of Hydroxylamine Derivatives on Imidochlorides. By HEINRICH LEY (*Ber.*, 1898, **31**, 240—246).—Tiemann's benzenylanilidoxime, $OH\cdot N{:}CPh\cdot NHPh$, is obtained by the action of hydroxylamine on benzanilidoimidochloride. The requisite quantity of sodium ethoxide (from 3·8 grams of metal) is added to a solution of hydroxylamine hydrochloride (11·5 grams) in absolute alcohol. The hydroxylamine solution, after the removal of the sodium chloride, is added to a solution of benzanilidoimidochloride (14 grams) in absolute alcohol, and the mixture allowed to remain for several hours. The solvent is then distilled off, and the product precipitated with water; after recrystallisation from dilute alcohol, it melts at 138° (Müller, Abstr., 1886, 875, gives 136°). No trace of the isomeric compound,

$$OH\cdot NH\cdot CPh{:}NPh,$$

is formed.

Stieglitz's benzenylorthotoluidoxime may be obtained in a similar manner from benzorthotoluidimidochloride.

Benzenylparachloranilidoxime crystallises in colourless needles or plates, melts at 183°, and gives a blue coloration with ferric chloride. It is readily soluble in acetone or hot alcohol, and only sparingly in light petroleum.

Parachlorobenzanilidimidochloride crystallises in long needles melting

at 68°. The *imidochloride* from benzoylorthonitraniline melts at 67—68°, and yields an *oxime* crystallising in yellow plates which melt and decompose at 187°. α-Benzylhydroxylamine reacts with benzanilidimidochloride, yielding the same product as is formed when benzenylanilidoxime is benzylated.

β-Benzylhydroxylamine, in perfectly neutral absolute alcoholic solution, also reacts with benzanilidimidochloride; the crystalline product $NPh\!:\!CPh\cdot N(C_7H_7)\cdot OH$, after being freed from oil and recrystallised from dilute alcohol or benzene, forms small, white, glistening needles melting at 148°. Its alcoholic solution gives a deep blue coloration with ferric chloride, and its ethereal solution a brownish-red. The oximes described above show the same colorations with ferric chloride. The compound exhibits many of the properties of Bamberger's azohydroxyamides.

Stieglitz (Abstr., 1890, 254) has previously shown that diazonium salts do not react with anilidoximes; the author finds that a reaction readily takes place in alkaline solution. Aniline (0·9 gram) is dissolved in normal hydrochloric acid (25 c.c.) and diazotised with the requisite quantity of sodium nitrite, and the strongly cooled diazonium solution is added to a solution of benzenylanilidoxime (2 grams) in excess of sodium hydroxide and kept at −5°. The yellow precipitate thus obtained may be recrystallised from alcohol, but the greater part undergoes decomposition during the process; it forms minute needles decomposing at 155—160°, and is probably the *sodium* salt of the compound,

$$OH\cdot N\!:\!CPh\cdot NPh\cdot N_2Ph \text{ or } NPh\!:\!CPh\cdot N(OH)\cdot N_2Ph.$$

It dissolves in acids, yielding colourless solutions, but is probably hydrolysed at the same time. J. J. S.

Stability of the Six Xylylsuccinimides. By Arturo Miolati and Alfredo Lotti (*Real. Accad. Linc.*, 1896, [v], 5, i, 88—96).—The authors have determined the velocity constants *Ac*, of hydrolysis of the isomeric xylylsuccinimides, $C_6H_3Me_2\cdot N<\begin{matrix}CO\cdot CH_2\\ |\\ CO\cdot CH_2\end{matrix}$, by soda, with the results summarised in the accompanying table; these substances, which have not previously been prepared, boil at above 300° without decomposition, and crystallise well.

Me : Me : $N(CO\cdot CH_2)_2$.	*Ac.*	Melting point.
1:3:2	0·1571	187°
1:2:3	0·8147	105
1:3:4	0·8653	118
1:4:5	0·8757	120
1:3:5	1·145	168
1:2:4	1·270	150

The imides can be divided into three groups according to the above velocity constants. The first group consists of the 1 : 3 : 2 isomeride, which has a small velocity constant, and in which both methyl groups are in ortho-positions relatively to the imido-group; the second group consists of the 1 : 2 : 3, 1 : 3 : 4, and 1 : 4 : 5 isomerides, which have

velocity constants of the same order, and in these one methyl group is ortho- to the imidogen; in the third group, consisting of the 1 : 3 : 5 and 1 : 2 : 4 derivatives, no methyl group is in the ortho-position relatively to the imido-group, and these have appreciably higher velocity constants. W. J. P.

Condensation Products of Piperonal, Vanillin, and Protocatechuic Aldehyde. By M. ROGOFF (*Ber.*, 1898, **31**, 175—176).—Piperonal, vanillin, and protocatechuic aldehyde readily form condensation products with amidophenols and their ethers. The *product* obtained from piperonal and paramidophenol is a crystalline powder melting at 208—209°, whilst that from paranisidine crystallises in colourless needles and melts at 121°. Vanillin and paramidophenol yield a *compound* which is a brown, crystalline powder melting at 203°, whilst the *product* obtained from paranisidine crystallises in colourless prisms and melts at 137°. The product from protocatechuic aldehyde and paramidophenol has not yet been obtained pure, but the corresponding compound with paranisidine forms glistening, golden-yellow crystals, and melts at 161—161·5°. A. H.

Base of Hypnoacetin and its Derivatives. By G. VIGNOLO (*Real. Accad. Linc.*, 1897, [v], **6**, i, 70—77 and 122—127).—Acetophenoneparacetamidophenol or hypnoacetin,

$$COPh\cdot CH_2\cdot O\cdot C_6H_4\cdot NHAc,$$

(Abstr., 1897, i, 617), is prepared by heating, in a reflux apparatus, a mixture of an alcoholic solution of monobromacetophenone with a solution of paracetamidophenol in alcoholic potash, hypnoacetin separating on cooling. It crystallises in transparent, six-sided scales, melting and decomposing at 160°, and is hydrolysed by hot hydrochloric acid with production of *acetophenoneparamidophenol*, $COPh\cdot CH_2\cdot O\cdot C_6H_4\cdot NH_2$, which separates on adding alkali, and crystallises in fine needles melting at 95°; its *hydrochloride*, which separates on boiling hypnoacetin with hydrochloric acid, crystallises in fine needles melting at 201° with decomposition; the acid *sulphate*,

$$COPh\cdot CH_2\cdot O\cdot C_6H_4\cdot NH_2,H_2SO_4,H_2O,$$

crystallises in prisms melting and decomposing at 188° and the normal *sulphate* crystallises, with $1H_2O$, in thin scales melting at 210°. The *nitrate* crystallises in needles or laminæ melting and decomposing at 160°, whilst the *picrate* is a yellow, crystalline powder melting at 177°. The *benzoyl* derivative, $COPh\cdot CH_2\cdot O\cdot C_6H_4\cdot NHBz$, crystallises in white needles melting at 166°; the *oxime*,

$$NOH{:}CPh\cdot CH_2\cdot O\cdot C_6H_4\cdot NH_2,$$

crystallises in needles and the *hydrazone* forms small, yellowish crystals melting at 128°.

On heating a mixture of acetophenoneparamidophenol, sodium acetate, and ethylenic dibromide in a reflux apparatus, at a temperature not higher than 145°, for 2 hours, extracting with water, and crystallising the residue from chloroform, *diparoxyacetophenonediphenylpiperazine*,

$$COPh\cdot CO\cdot CH_2\cdot O\cdot C_6H_4\cdot N{<}{\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}}{>}N\cdot C_6H_4\cdot O\cdot CH_2\cdot COPh,$$

is obtained as a white, crystalline powder melting at 175°.

Paroxyacetophenonephenylcarbamide,

$$NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot COPh,$$

prepared by the action of potassium cyanate on acetophenoneparamidophenol hydrochloride in aqueous solution, crystallises in slender needles melting and decomposing at 160°; it is tasteless, and is physiologically inactive.

Hypnoacetin administered internally to the human subject has an antipyretic action and analgesic and hypnotic properties; its effects, however, are not always uniform, and it is innocuous in doses of 0·25—1 gram per day.

The physiological effects of acetophenoneparamidophenol administered hypodermically to animals have been investigated; it is rapidly eliminated in the urine. W. J. P.

Some Mono- and Di-halogen Ketones. By Franz Kunckell and Friedrich Johannssen (*Ber.*, 1898, 31, 169—172. Compare Abstr., 1897, i, 522).—Parahydroxychloracetophenone (parachloracetylphenol), $CH_2Cl\cdot CO\cdot C_6H_4\cdot OH$, cannot be obtained by the action of chloracetic chloride on phenol, but is readily formed when anisoil is treated with the chloride in presence of aluminium chloride; it crystallises in reddish plates, melts at 148°, and readily dissolves in dilute aqueous soda and in alcohol. *Paramethoxyphenacylparaphenetidine*, $OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot OEt$, formed by the action of anisyl chloromethyl ketone on phenetidine, crystallises in pale yellow plates melting at 124°; by nitric acid, it is converted into a *mononitro*-compound, which crystallises in red plates and melts at 171°. *Parachloranisyl chloromethyl ketone*, prepared from parachloranisoil, melts at 71°, whilst the corresponding *parabromanisyl chloromethyl ketone* crystallises in white needles melting at 94°. *Chloracetylphenylic parabromethylic ether*, $CH_2Cl\cdot CO\cdot C_6H_4\cdot O\cdot C_2H_4Br$, prepared from phenylic bromethylic ether, forms small, hard, yellowish-white crystals melting at 104°. *Dichloracetyldiphenylic ethylenic ether*,

$$(CH_2Cl\cdot CO\cdot C_6H_4\cdot OCH_2)_2,$$

is prepared in a similar manner from diphenylic ethylenic ether, and forms a white mass melting at 160—165°.

Phenylic dichloracetate, prepared by the action of dichloracetic chloride on phenol in the presence of aluminium chloride, forms white plates melting at 33°. *Paradichloracetylanisoil*,

$$CHCl_2\cdot CO\cdot C_6H_4\cdot OMe,$$

crystallises in colourless needles, melting at 75—76°, whilst *dichloracetylphenetoil* forms reddish plates melting at 73°. *Dichloracetyl-α-naphthylic methylic ether*, $CHCl_2\cdot CO\cdot C_{10}H_6\cdot OMe$, crystallises in long, white needles melting at 100°, whilst the corresponding ethylic ether crystallises in white, compact needles melting at 110°. A. H.

Some Brominated Ketones. By Franz Kunckell and Wilhelm Scheven (*Ber.*, 1898, 31, 172—174. Compare the foregoing abstract). —The following compounds have been obtained by acting on phenol and its ethers with bromacetic bromide in the presence of aluminium chloride. *Phenylic bromacetate*, $CH_2Br\cdot COOPh$, crystallises in white, lustrous plates melting at 32°. Anisoil yields *anisyl parabromomethyl ketone*, $CH_2Br\cdot CO\cdot C_6H_4\cdot OMe$, which crystallises in white needles

melting at 73°, whilst if double the quantity of the bromide and aluminium chloride be employed, *anisyl di-bromomethyl diketone*, $(CH_2Br\cdot CO)_2C_6H_3\cdot OMe$, is formed; this crystallises in yellowish-white needles melting at 79—80°; *phenetyl parabromomethyl ketone* also forms white needles and melts at 59—60°, whilst *phenetyl di-bromomethyl diketone* crystallises in hard, reddish needles melting at 77°. *Bromacetyl-α-naphthylic methylic ether*, $CH_2Br\cdot CO\cdot C_{10}H_6\cdot OMe$, crystallises in greenish needles melting at 70°, whilst the corresponding *ethylic* ether forms yellowish-white needles and melts at 119°. A. H.

Action of Sodium Ethoxide on Ethylic αβ-Dibromophenylpropionate, Ethylic Citradibromopyrotartrate, and Ethylic αβ-Dibromopropionate. By VIRGIL L. LEIGHTON (*Amer. Chem. J.*, 1898, **20**, 133—148).—This work is an extension of that of Michael and Bucher on the action of sodium ethoxide on ethylic dibromosuccinate (Abstr., 1896, i, 85 and 599); when an excess of the former (20 per cent. more than that calculated for 2 mols. of sodium ethoxide) is left in contact, during 3 days, with ethylic αβ-dibromophenylpropionate in alcoholic solution, small quantities of phenylpropiolic acid and *ethylic diethoxyphenylpropionate*, $CPh(OEt)_2\cdot CH_2\cdot COOEt$, are formed, together with a much larger proportion of *ethylic β-ethoxycinnamate*,

$$OEt\cdot CPh\colon CH\cdot COOEt.$$

When slightly impure, ethylic diethoxyphenylpropionate boils at 146—148° under 10 mm. pressure, and is converted by cold 4 per cent. alcoholic potash into benzoylacetic acid. *Ethylic β-ethoxycinnamate* boils at 154—155° under 9 mm. pressure, and is converted by boiling 4 per cent. alcoholic potash into *β-ethoxycinnamic acid*, which separates from carbon tetrachloride in slender, transparent crystals, and melts at 164—165°. The *silver* salt, $C_{11}H_{11}O_3Ag$, is a white, microcrystalline powder, whilst the *calcium* salt, with $8H_2O$, crystallises from water in white needles. On being left in contact with concentrated hydrochloric acid (sp. gr. = 1·2), both β-ethoxycinnamic acid and its ethylic salt are converted into benzoylacetic acid.

When an excess (20 per cent. more than 2 molecular proportions) of sodium ethoxide is left in contact with ethylic citradibromopyrotartrate dissolved in alcohol, *ethylic ethoxycitraconate* is formed, together with a larger quantity of *ethylic diethoxypyrotartrate*. The former compound boils at 140° under 15 mm. pressure, and is converted by cold 4 per cent. alcoholic potash into *ethoxycitraconic acid*,

$$COOH\cdot CMe\colon C(OEt)\cdot COOH,$$

a thick, viscous oil; the *barium* salt, with H_2O, is precipitated on adding alcohol to its aqueous solution; the *ethylic* salt, when boiled with 10 per cent. sulphuric acid, is converted into propionylformic acid. *Ethylic diethoxypyrotartrate*, $COOEt\cdot CH(OEt)\cdot CMe(OEt)\cdot COOEt$, boils at 157° under 15 mm. pressure, and is converted by dilute caustic potash into *diethoxypyrotartaric* acid, a thick oil, which yields a white, crystalline *silver* salt, $C_9H_{13}O_6Ag_2$, and an insoluble *lead* salt; all the other metallic salts are very soluble in water.

When alcoholic sodium ethoxide reacts with ethylic αβ-dibromopropionate, a mixture of *ethylic ethoxyacrylate* and *ethylic diethoxypropionate* is formed. W. A. D.

Action of Acetic Anhydride on Phenylpropiolic Acid. By ARTHUR MICHAEL and JOHN E. BUCHER (*Amer. Chem. J.*, 1898, **20**, 89—120).—The action of acetic anhydride on phenylpropiolic acid is not analogous to its action on acetylenedicarboxylic acid; whereas, in the latter case, acetoxymaleic anhydride is obtained (Abstr., 1896, i, 85), the former reaction yields 1-*phenylnaphthalene*-2 : 3-*dicarboxylic anhydride*; this crystallises from cumene in transparent prisms, and, when heated, softens at 230° and melts at 255°. It dissolves in a boiling 10 per cent. solution of sodium hydroxide, and, on cooling, white, shining plates of *sodium* 1-*phenylnaphthalene*-2 : 3-*dicarboxylate*, $C_{18}H_{10}O_4Na_2 + 4\frac{1}{2}H_2O$, separate. The corresponding *barium* salt crystallises with $4H_2O$, and yields α-phenylnaphthalene when distilled with barium hydroxide; the *calcium* salt crystallises with $3H_2O$, whilst the *silver* salt is anhydrous, and is not affected by light. The *methylic* salt, $C_{16}H_{10}(COOMe)_2$, crystallises from alcohol in white prisms, melts at 118—120°, and is easily soluble in hot methylic and ethylic alcohols, and carbon tetrachloride, and less soluble in ether. No acid exists corresponding with these salts; on decomposing solutions of the metallic salts with acids, the anhydride, $C_{18}H_{10}O_3$, is immediately formed. By the action of aniline on this anhydride, a *compound*, $C_{18}H_{10}O_3,NH_2Ph$, is obtained, which separates from alcohol in transparent crystals and melts at 194° with decomposition.

On reducing sodium 1-phenylnaphthalene-2 : 3-dicarboxylate with sodium amalgam, and subsequently acidifying the solution with sulphuric acid, an *acid*, $C_{18}H_{16}O_4$, is obtained; this forms white crystals, melts and decomposes at 200—202°, and is easily soluble in acetone and ethylic acetate, but insoluble in carbon tetrachloride and benzene, and probably has the constitution of a 1-*phenyltetrahydronaphthalene*-2 : 3-*dicarboxylic acid.* The *silver* salt, $C_{18}H_{14}O_4Ag_2$, is a white, crystalline powder; the *anhydride*, $C_{18}H_{14}O_3$, obtained by heating the acid with acetic anhydride, melts at 145—150°.

When the anhydride of 1-phenylnaphthalene-2 : 3-dicarboxylic acid is reduced by zinc dust in acetic acid solution, a *lactone*,

$$C_6H_4{<}\begin{matrix}CPh{:}C{-}CO\\ \quad\;\;| \\ CH : C{\cdot}CH_2\end{matrix}{>}O,$$

is obtained, which crystallises from alcohol and melts at 135—137°.

1-*Phenylbenzene*-2 : 3 : 5 : 6-*tetracarboxylic acid*, obtained on oxidising 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride with alkaline potassium permanganate, is a white, crystalline substance which has no definite melting point; the *silver* salt, $C_{12}H_6(COOAg)_4$, and the *lead* salt, are amorphous powders, insoluble in water; the *barium* salt, containing $8H_2O$, is crystalline, and is less soluble in hot water than in cold; the *calcium* salt is easily soluble in water; the *methylic* salt crystallises from carbon tetrachloride in large transparent rhombohedra, melts at 130—133°, and is soluble in hot alcohol and chloroform, whilst the *benzylic* salt is a white, crystalline substance which melts at 114—118°. The *anhydride* of the acid is a light yellow, crystalline compound, soluble in boiling xylene. When the barium salt is distilled with barium hydroxide, diphenyl is obtained.

An *acid*, apparently isomeric with the foregoing, is formed along with it when 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride is

oxidised by potassium permanganate; it is amorphous, and yields an amorphous *barium* salt, which is very soluble in water and is converted into diphenyl when distilled with barium hydroxide; the *silver* salt, $C_{12}H_6(COOAg)_4$, and the *methylic* salt, $C_{12}H_6(COOMe)_4$, are also both amorphous. The constitution of the acid is uncertain, and its formation cannot be explained by theory.

In the light of the above results, the authors discuss the formation of the isatropic acids from atropic acid; this appears to be analogous to the formation of 1-phenylnaphthalene-2 : 3-dicarboxylic acid from phenylpropiolic acid. The analogy supports the view taken by Fittig (Abstr., 1881, 425), that the isatropic acids are 1-phenyltetrahydronaphthalene-1 : 4-dicarboxylic acids. The constitution of atronic and isatronic acids is discussed; to atronol, the constitution of a dihydrophenylnaphthalene is attributed, whilst atronylene and its sulphonic acid are considered to be α-phenylnaphthalene and its sulphonic acid respectively.

W. A. D.

Action of Caustic Alkalis on Phthalides. By PIETRO GUCCI (*Real. Accad. Linc.*, 1897, [v], 6, i, 295—298).—On gradually heating diethylphthalide with caustic soda and a little water to 300°, diethyl ketone distils, whilst sodium benzoate with a little phthalate remains in the residue; with caustic potash, a better yield of the phthalate and a poorer one of the ketone is obtained. Diethylphthalide, therefore, behaves like dimethylphthalide towards caustic alkalis.

W. J. P.

Dimorphism of α-Monomethylic Hemipinate. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1897, 18, 589—597).—The more stable modification at ordinary temperatures melts at 138°. From ether, anorthic crystals were obtained containing $1H_2O$; these melted at 134·5—136·5°, and gave $a:b:c = 0·9105:1:1·0269$; $\alpha = 112° 27'$, $\beta = 102° 2'$, $\gamma = 95° 25'$. When crystallised from water, this modification is converted into the one which melts at 120—122°, but this form, on being rubbed with a trace of the compound of higher melting point, is reconverted into the modification which melts at 138°. The two forms are apparently enantiotropic. Anorthic crystals containing $1H_2O$, were grown from an ethereal solution of the substance containing a crystal of the modification of lower melting point. They melted at 118—120°, and gave $a:b:c = 0·9342:1:0·9941$; $\alpha = 107° 45'$, $\beta = 101° 50'$, $\gamma = 107° 40'$. Both modifications give the same reaction with ferric chloride.

W. A. D.

Action of Alcoholic Potassium Sulphide and Hydrosulphide on Symmetrical Dibromosulphones. By JULIUS TROEGER and V. HORNUNG (*J. pr. Chem.*, 1897, [ii], 56, 445—469).—The dibromide, $R\cdot SO_2\cdot CH_2\cdot CHBr\cdot CH_2Br$, was usually mixed with a little alcohol, treated with excess of a strong alcoholic solution of potassium sulphide (1 c.c. = 0·225 K_2S) or hydrosulphide, and the mixture either allowed to remain or heated on the water bath. With potassium sulphide, a sulphide, $R\cdot SO_2\cdot CH_2\cdot CH<\begin{matrix}S\\|\\CH_2\end{matrix}$, was formed, as a rule; and this, in

acetic acid solution, could be oxidised by potassium permanganate to a disulphone, $R\cdot SO_2\cdot CH_2\cdot CH<\begin{matrix}SO_2\\|\\CH_2\end{matrix}$. With potassium hydrosulphide, impure yellow or reddish oils were obtained, and it was impossible to decide whether these were mixtures of a dihydrosulphide,

$$R\cdot SO_2\cdot CH_2\cdot CH(SH)\cdot CH_2\cdot SH,$$

with a sulphide, or whether polymerisation had taken place. With amylic and phenylic hydrosulphides, in the presence of an equivalent amount of sodium ethoxide, they did react, yielding compounds of the type, $R\cdot SO_2\cdot CH_2\cdot CH(SR^1)\cdot CH_2\cdot SR^1$, which could be oxidised to trisulphones, $R\cdot SO_2\cdot CH_2\cdot CH(SO_2\cdot R^1)\cdot CH_2\cdot SO_2\cdot R^1$; these compounds were all oils, except $SO_2Ph\cdot CH_2\cdot CH(SPh)\cdot CH_2\cdot SPh$, which is crystalline (Otto, Abstr., 1895, i, 230). The dibromides experimented with were those of phenylallyl-, paratolylallyl-, orthotolylallyl-, β-naphthylallyl-, and α-naphthylallyl-sulphones [$R = Ph$; C_6H_4Me; $C_{10}H_7$]. In the one case of phenylallylsulphone dibromide and potassium sulphide, the reaction is abnormal; the product, which melts at 157—158°, appears to have the constitution $\left[SO_2Ph\cdot CH_2\cdot CH<\begin{matrix}S\\|\\CH_2\end{matrix}\right]_2O$; when oxidised, it yields the disulphone, $SO_2Ph\cdot CH_2\cdot CH<\begin{matrix}SO_2\\|\\CH_2\end{matrix}$, a crystalline powder which is still unmelted at 230°. The well-characterised substances obtained in the investigation are enumerated below, with their melting points; of those obtained only as oils, no further mention is made.

Phenylallyl derivatives.—$(SO_2Ph\cdot C_3H_5{:}S)_2O$, 157—158°; $SO_2Ph\cdot C_3H_5{:}SO_2$, above 230°; $SO_2Ph\cdot C_3H_5(SO_2\cdot C_5H_{11})_2$, 120°. *Paratolylallyl derivatives.*—$C_6H_4Me\cdot SO_2\cdot C_3H_5{:}S$, 180—181°; $C_6H_4Me\cdot SO_2\cdot C_3H_5{:}SO_2$, above 200°; $C_6H_4Me\cdot SO_2\cdot C_3H_5(SO_2\cdot C_5H_{11})_2$, 112—113°; $C_6H_4Me\cdot SO_2\cdot C_3H_5(SO_2Ph)_2$, 88·5°. *Orthotolylallyl derivatives.*—None well characterised. *β-Naphthylallyl derivatives.*—$C_{10}H_7\cdot SO_2\cdot C_3H_5{:}S$, amorphous; $C_{10}H_7\cdot SO_2\cdot C_3H_5(SO_2\cdot C_5H_{11})_2$, 136°. *α-Naphthylallyl derivatives.*—$C_{10}H_7\cdot SO_2\cdot C_3H_5{:}S$, amorphous.

C. F. B.

Condensation Products of Aldehydes with Phenols and Phenolic Acids. By LEOPOLD KAHL (*Ber.*, 1898, 31, 143—151).—Baeyer and others have shown that formaldehyde reacts with phenols in the proportion of one molecule of aldehyde to two of the phenol.

Caro's methylenedipyrogallol (Abstr., 1892, 856) is best obtained by the following method. A solution of pyrogallol (50 grams) in water (250 c.c.) is mixed with 15 grams of a 40 per cent. solution of formaldehyde, and concentrated hydrochloric acid (about 125 c.c.) is added to the mixture until no further precipitate is obtained, care being taken that the whole is well stirred. When the dry compound is dissolved in about 10 times its weight of concentrated sulphuric acid, kept in a stoppered vessel for 24 hours, and then exposed to the air in an open dish, *formopyrogallaurin*,

$O{:}C_6H_2(OH)_2{:}CH\cdot C_6H_2(OH)_3$ [$O:(OH)_5 = 4:3:5$; $3':4':5'$], is deposited in the form of black, opaque, crystalline aggregates. It is best purified by dissolving it in boiling water and precipitating with hot, alcoholic hydrogen chloride. It readily dissolves in alkalis, yielding green solutions, and in alkali carbonates, yielding brown solutions.

A *compound*, $C_{16}H_{16}O_6 + \frac{1}{2}H_2O$, is obtained when a solution of pyrogallol (50 grams) in water (200 c.c.) is mixed with acetaldehyde (8·8 grams) and hydrochloric acid (125—150 c.c.), and then warmed on the water bath until no further precipitate is obtained. When recrystallised from 50 per cent. alcohol, it forms colourless needles or prisms sparingly soluble in absolute alcohol, ether, acetone, methylic alcohol, and ethylic acetate, and dissolves slowly in alkali carbonates, readily in alkalis, but not in concentrated sulphuric acid; when heated, it decomposes without melting, and does not yield a dye.

Methylenedinaphthoresorcinol, $CH_2[C_{10}H_5(OH)_2]_2$, after drying at 130°, forms a colourless, crystalline powder, composed of irregular plates; it crystallises from boiling water in needles, melts at 164·5°, and is readily soluble in alcohol, ether, acetic acid, or alkalis. It dissolves in cold, concentrated sulphuric acid, yielding *formaldehydehydroxynaphthofluorone*, $O{:}C_{10}H_5{<}^{CH}_{-O-}{>}C_{10}H_5\cdot OH$, which is deposited, as the solution becomes dilute, in the form of small, opaque, brownish crystals; this may be purified by recrystallisation from acetic acid, in which it dissolves, yielding a yellow solution with a green fluorescence, but it is insoluble in ether, benzene, or acetone.

A theoretical yield of methylenedisalicylic acid is obtained by Geigy and Co.'s method (D. R. P. No. 49970); it can readily be obtained in crystalline form, is only sparingly soluble in water, but dissolves readily in alcohol or acetic acid. It melts at 242° (Geigy gives 238°). *Formaurindicarboxylic acid*, $COOH\cdot C_6H_3O{:}CH\cdot C_6H_3(OH)\cdot COOH$, is obtained when the above acid, dried at 120°, is dissolved in 10 times its weight of cold sulphuric acid and the solution, while kept quite cold, is treated with nitrosulphonic acid in amount corresponding with 1 mol. N_2O_3; on pouring the product into cold water, the dye is deposited in the form of orange-coloured flocks. It is best purified by conversion into its colourless sulphurous acid derivative, which can then be decomposed by warming with dilute acids. The *calcium*, *barium*, and *aluminium* salts are insoluble in water. *Methylenedicresotic acid* is obtained when orthocresotic acid (2 parts), 40 per cent. formaldehyde (1 part), and concentrated hydrochloric acid (8 parts) are heated on the water bath; it crystallises from alcohol or acetic acid in prisms, melts and decomposes at 276—277°, and is moderately soluble in ether.

When resorcylic acid (10 grams) is mixed with concentrated hydrochloric acid and acetaldehyde (1·42 grams), and the mixture allowed to remain for several days, a colourless, amorphous product, formed by the condensation of two molecules of the aldehyde with two of resorcylic acid and the removal of two molecules of water, is obtained. It is very sparingly soluble in water, more readily in alcohol, ether, acetic acid, or ethylic acetate, but cannot be obtained in a crystalline form; it decomposes when heated, but does not melt.

When gallic acid (100 grams) is covered with concentrated sulphuric acid and then treated with acetaldehyde (12·9 grams), condensation takes place slowly; at the end of 48 hours, the mixture is poured into water, the product boiled with water to remove unaltered gallic acid, and recrystallised several times from 50 per cent. alcohol. Prismatic crystals are thus obtained, which are soluble in alcohol, ether, alkalis, and alkali carbonates, and have the composition $C_{18}H_{14}O_9$.

Benzaldehyde and gallic acid yield a condensation product, $C_{28}H_{16}O_8$, which crystallises from 50 per cent. acetic acid in opaque, nodular crystals which are insoluble in water. J. J. S.

Products of the Action of Formaldehyde on Gallic Acid. By RICHARD MÖHLAU and LEOPOLD KAHL (*Ber.*, 1898, **31**, 259—266. Compare Caro, Abstr., 1892, 855).—Four methylenedigallic acids have been obtained by the action of formaldehyde on gallic acid.

(1) Sparingly soluble, crystalline methylenedigallic acid. Caro's method gives a 20 per cent. yield of this acid, but a 57 per cent. yield may be obtained by the following method. Hot concentrated hydrochloric acid (375 grams) and 40 per cent. formaldehyde solution (60 grams) are added to a hot solution of gallic acid (100 grams) in water (1125 grams) contained in a reflux apparatus and placed on a boiling water bath. The contents of the flask are kept well stirred during the mixing. When no more precipitate is formed, the mixture is cooled and filtered, the residue is well washed, boiled with water, and filtered while hot, and then washed with alcohol and ether to remove colouring matter. It is a light, crystalline powder which becomes strongly electric on rubbing, is extremely sparingly soluble in hot water, but dissolves somewhat more readily in dilute or absolute alcohol, from which it crystallises in long, white needles. Its alkaline solutions readily turn red on exposure to the air. When heated, it chars and decomposes without melting. The *anhydride*, $C_{15}H_{10}O_9$, probably $C_6H(OH)_3<\genfrac{}{}{0pt}{}{—CH_2—}{CO·O·CO}>C_6H(OH)_3$, is formed when a saturated alcoholic solution of the acid is boiled for some time; and the acid is completely converted into this anhydride when heated with 95 per cent. alcohol (5 parts) for an hour at 105° in sealed tubes. The anhydride is insoluble in water, alcohol, or ether, but soluble in concentrated sulphuric acid, yielding a yellow solution, and also in alkalis or alkali carbonates.

(2) A readily soluble crystalline methylenedigallic acid is deposited in the form of long, white needles when the hot aqueous washings from acid No. 1 are allowed to stand for some time. A better yield is obtained when 100 grams of gallic acid, 40 grams of formaldehyde solution, and 1500 grams of dilute hydrochloric acid (1 of acid to 4 of water) are heated for an hour on a briskly boiling water bath; the crude acid is filtered, washed with cold water until free from hydrogen chloride, and then extracted with boiling water; the yield is 30—40 per cent. It is moderately soluble in boiling water, readily in alcohol and ether, and when boiled with a quantity of water insufficient to dissolve it, together with a few drops of concentrated hydrochloric acid, it yields

an *anhydride*, $C_{30}H_{22}O_{19}$, which can also be obtained by heating the acid with water at 110° for 2—3 hours; it forms large, reddish-coloured, rhombic crystals.

A readily soluble, amorphous methylenedigallic acid (No. 3) is deposited when the aqueous extracts from Caro's acid are allowed to remain for a week; it is also obtained when acid No. 2 is kept for several months in dilute hydrochloric acid solution. It is fairly readily soluble in hot water, very readily in alcohol, and dissolves in concentrated sulphuric acid, yielding a reddish-brown solution. Its phenylhydrazine salt is readily soluble in alcohol, but cannot be obtained in a crystalline condition from this solvent. When the acid is boiled for some time with alcohol, it is converted into the anhydride, $C_{15}H_{10}O_9$, which forms minute, prismatic crystals. It is insoluble in water and alcohol, but dissolves in alkalis, and is not identical with the anhydride obtained from Caro's acid.

A sparingly soluble, amorphous methylenegallic acid (No. 4) is readily obtained by Kleeberg's method (Abstr., 1891, 1199); the crude acid is digested several times with hot water, in order to remove acid No. 3. It is also obtained when acid No. 3 is heated with formaldehyde and hydrochloric acid on the water bath. It is very sparingly soluble in alcohol, acetone, acetic acid, and benzene, but dissolves in alkalis and alkali carbonates. The acid and also the anhydride, $C_{30}H_{22}O_{19}$, have been previously described by Baeyer (this Journal, 1873, 501) and by Kleeberg (*loc. cit.*), who, however, ascribed somewhat different compositions to them.

Acids Nos. 1 and 2 are readily converted into acid No. 3, and this in its turn into acid No. 4. J. J. S.

Formaldehydetrihydroxyfluoronedicarboxylic Acid. By Richard Möhlau and Leopold Kahl (*Ber.*, 1898, 31, 266—271).—Ten grams of the sparingly soluble crystalline methylenedigallic acid (see previous abstract), previously dried at 100°, is dissolved in about 300 grams of concentrated sulphuric acid at a temperature below 70°, care being taken that the mass is kept well stirred; after cooling to the ordinary temperature, the requisite quantity of nitrosyl sulphate is added and the whole allowed to remain for 24 hours. The dye, $C_{15}H_8O_9$, may be obtained in a crystalline form by exposing the sulphuric acid solution to the atmosphere in flat dishes; it may also be precipitated by adding first diluted sulphuric acid (1 : 1) carefully so that the temperature does not rise above 35°, and then a still more dilute solution (1 : 10). It is a violet, crystalline powder, but sparingly soluble in boiling water, and practically insoluble in the usual solvents; it dissolves in concentrated sulphuric acid but does not yield a fluorescent solution. It forms sparingly soluble *lakes* with metallic oxides; *calcium* and *barium* salts form blue, flocculent precipitates. When heated with anhydrous sodium acetate and acetic anhydride, the acid yields an *acetyl* derivative,

$$\begin{array}{l} COOH\cdot C_6H(OAc)_2\cdot CH\text{——}O \\ \;\;\;\;\;\;\;\;\;\;\; | \; | \\ \;\;\;\;\;\;\;\;\; O\text{————————}C_6H(OAc)_2 \end{array} \!\!> CO,$$

which crystallises from alcohol in colourless, glistening plates melting at

140·5—141·5°; this is sparingly soluble in most solvents, dissolves to a colourless solution in sulphuric acid, but this gradually turns red, probably owing to hydrolysis. A *benzoyl* derivative, $C_{43}H_{24}O_{13}$, was also obtained by the aid of benzoic chloride; after dissolution in hot benzene and precipitation with hot alcohol, it forms large crystals melting at 250·5—252·5°. Formaldehydetrihydroxyfluoronedicarboxylic acid, when reduced with sodium carbonate and glucose, yields *tetrahydroxyxanthendicarboxylic acid*,

$$COOH\cdot C_6H(OH)_2{<}^{CH_2}_{-O-}{>}C_6H(OH)_2\cdot COOH \; [COOH:(OH)_2 = 1:3:4 \text{ and } 1':3':4'].$$

After several crystallisations from dilute alcohol (50 per cent.), it is obtained in spherical aggregates of prisms. Its solution in concentrated sulphuric acid turns cherry red on the addition of sodium hydroxide. When heated, it decomposes without melting, and when distilled with zinc dust yields xanthen. Its *tetracetyl* derivative, after recrystallisation from 50 per cent. acetic acid, forms glistening, colourless plates melting at 241°. J. J. S.

Phthaleins of Orthosulphobenzoic Anhydride. By M. D. Sohon (*Amer. Chem. J.*, 1898, **20**, 127—129).—*Dimethylanilinesulphonphthalein*, $SO_2{<}^{C_6H_4}_{-O-}{>}C(C_6H_4\cdot NMe_2)_2$, prepared by heating a mixture of dimethylaniline (2 mols.), orthosulphobenzoic anhydride (1 mol.), and phosphorus oxychloride on the water bath for a short period, is a bluish-black, brittle substance which dissolves in hot water giving a bright blue solution that dyes silk or wool the same colour. It is soluble in alcohol, but insoluble in ether, benzene, light petroleum, and chloroform; in dilute hydrochloric acid, it dissolves, giving a green solution which becomes yellow when excess of acid is added, and pink on the addition of alkali. The sulphonphthalein is not affected by reducing agents.

Diethylanilinesulphonphthalein possesses similar properties to those of the methyl compound. W. A. D.

Preparation of Phenylrosinduline. By Ludwig Paul (*Chem. Centr.*, 1897, i, 1168; from *Chem. Rund.*, 1897, 146—147).—The author describes the following new method of preparing phenylrosinduline. 5·8 grams of dry paranitrobenzeneazo-α-naphthylamine and 15 grams of aniline are kept at 160—165° for 2 hours in an oil bath, and the product boiled with dilute hydrochloric acid; the insoluble residue is then dissolved in boiling alcohol of 94° (Tralles), the solution filtered after 24 hours, and decomposed with sodium hydroxide solution. When purified by washing with alcohol of 50°, dissolving in alcohol of 94° and decomposing with sodium hydroxide, the phenylrosinduline melts at 229—230°.

If the above mixture is kept at 190—200° for 5 hours, the product obtained is not completely soluble in a solution of hydrochloric acid in alcohol, and gives a poorer yield of phenylrosinduline of a lower melting point and a bluer shade. By the action of 10 grams of aniline on 5 grams of benzeneazo-α-naphthylamine hydrochloride at 160° for 8

hours, only 2·5 grams of phenylrosinduline was obtained; it melted at 225° and had a darker colour (compare Fischer and Hepp, Abstr., 1888, 1291). E. W. W.

Oxidation of Naphthalene by Potassium Permanganate. By JOSEPH TCHERNIAC (*Ber.*, 1898, **31**, 139).—A reply to Procházka (this vol., i, 201). The author states that he has already given details for the oxidation of naphthalene by permanganate and also by manganate in his patent specifications. J. J. S.

Naphthalene- and Orthotoluene-thiosulphonic Acids. By JULIUS TROEGER and W. GROTHE (*J. pr. Chem.*, 1897, [ii], **56**, 470—475).—The potassium salts of these acids, $R\cdot SO_2\cdot SK$, are obtained by adding the sulphonic chloride, $R\cdot SO_2Cl$, gradually to alcoholic potassium sulphide, warming at first; the solution is filtered from the potassium chloride and evaporated to crystallisation; it is difficult to obtain a product quite free from potassium chloride. The thiosulphonates of *a*- and *β*-naphthalene and of orthotoluene were prepared [$R = C_{10}H_7$; C_6H_4Me]. C. F. B.

Constituents of Oil of Roses and Allied Ethereal Oils. By JULIUS BERTRAM and EDUARD GILDEMEISTER (*J. pr. Chem.*, 1897, [ii], **56**, 506—514).—A reply to H. Erdmann (this vol., i, 36, 37). It is shown that geraniol, as issued by Schimmel of Leipzig, does not contain chlorine compounds, and it is argued that *geraniol* is preferable to *rhodinol* as a name for the constituent $C_{10}H_{18}O$ common to oil of roses and oil of geranium. C. F. B.

Rhodinol. By THEODOR POLECK (*Ber.*, 1898, **31**, 29—30).—The author protests against the use of the term rhodinol for *l*-citronellol, $C_{10}H_{20}O$ (Tiemann and Schmidt, Abstr., 1896, i, 384); he had already applied it to a substance, $C_{10}H_{18}O$, which occurs in German and Turkish rose-oil (Abstr., 1891, i, 323). C. F. B.

The Rhodinol Question. By THEODOR POLECK (*J. pr. Chem.*, 1897, [ii], **56**, 515—519. Compare H. Erdmann, this vol., i, 37, and preceding abstract).—The use of *rhodinol* is advocated as a name for the constituent $C_{10}H_{18}O$ common to oil of roses and oil of geranium.
C. F. B.

Camphoronic Acid, Camphoranic Acid, and *β*-Hydroxycamphoronic Acid. By JULIUS BREDT (*Annalen*, 1897, **299**, 131—160. Compare Abstr., 1896, i, 653).—Bromanhydrocamphoronic chloride (Abstr., 1895, i, 242) crystallises in the monosymmetric system; $a : b : c = 0·75904 : 1 : 0·78082$, $\beta = 87° 53'$. *a*-Methylic bromanhydrocamphoronate crystallises in the rhombic system; $a : b : c = 0·91366 : 1 : 1·0434$. The *β*-methylic salt (m. p. 142°) separates from ether in crystals belonging to the same system; $a : b : c = 0·69502 : 1 : 0·42516$.

Dimethylic camphoranate separates from methylic alcohol in crystals belonging to the rhombic system; $a : b : c = 0·91153 : 1 : 0·70741$. The methylic hydrogen salt crystallises from water in the same system and contains $1H_2O$; $a : b : c = 0·6523 : 1 : 0·72565$. The anhydrous salt separates from ether in tetragonal crystals; $a : c = 1 : 1·9458$.

The paper gives a detailed account of compounds already described by the author (*loc. cit.*). M. O. F.

Isoacetophorone and Camphorone. By JULIUS BREDT and REINHARD RÜBEL (*Annalen*, 1897, **299**, 160—192. Compare Kerp, Abstr., 1896, i, 447).—Kerp has shown that camphorone, the ketone, $C_9H_{14}O$, obtained by distilling calcium camphorate, is not identical with the isomeric substance produced from acetone under the influence of sodium ethoxide. The authors have independently arrived at the same conclusion, and find that the ketone has the same properties whether prepared by the action of quicklime or of sodium ethoxide. This ketone, which Kerp called isophorone, the authors refer to as *isoacetophorone*, with the double purpose of indicating its origin, and avoiding confusion with isocamphorone.

Isoacetophorone *phenylhydrazone*, $C_{15}H_{20}N_2$, crystallises from dilute alcohol in long, pale yellow needles, and melts at 68°. It is very unstable, and rapidly becomes brown on exposure to the air. Isoacetophorone yields two oximes, melting at 75° and 100°; these have been described by Kerp (*loc. cit.*) and Tissier respectively. The former crystallises in the hexagonal system; $a:c = 1:0·4676$. The latter forms triclinic crystals; $a:b:c = 0·9930:1:0·6502$. $\alpha = 115° 36\frac{1}{2}'$, $\beta = 101° 56'$, $\gamma = 98° 26'$.

When isoacetophorone is suspended in water, and oxidised with potassium permanganate, it yields the monobasic acid, $C_9H_{14}O_4$, the ketonic acid, $C_8H_{14}O_3$, the lactone, $C_8H_{12}O_2$, and the dibasic acid, $C_6H_{10}O_4$.

The *acid*, $C_9H_{14}O_4$, is obtained by repeated distillation of the fraction of the oxidation product which boils at 195—210° under a pressure of 14 mm.; it melts at 99—100°. The acid separates alike from water and from a mixture of ether and light petroleum, in large, transparent, hemimorphic crystals belonging to the rhombic system; $a:b:c = 0·6749:1:1·1016$. The *calcium* salt crystallises from water, and contains $2H_2O$.

The ketonic *acid*, $C_8H_{14}O_3$, is derived from the fraction which boils at 125—150° under a pressure of 14 mm.; the *calcium* salt crystallises from water and contains $1H_2O$. The *ethylic* salt boils at 104° under a pressure of 14 mm. The *oxime* dissolves readily in organic solvents excepting light petroleum.

The *lactone*, $C_8H_{12}O_2$, is obtained from the portion of the oxidation product which boils at 75—100° under a pressure of 14 mm. Treatment with boiling, concentrated alkalis regenerates the ketonic acid, from which it is derived by elimination of the elements of water.

The *acid*, $C_6H_{10}O_4$, crystallises from water, and melts at 139—140°. It is dibasic, and the *anhydride* boils at 104° under a pressure of 11 mm. The *anilic acid* (compare Abstr., 1897, i, 267) crystallises in lustrous leaflets; the *anil* crystallises from alcohol in prismatic needles, and melts at 85—86°.

Further oxidation of the ketonic acid, $C_8H_{14}O_3$, in alkaline solution with potassium permanganate gives rise to unsymmetrical dimethylsuccinic acid.

The authors represent the constitution of acetophorone (m. p. 28°)

by the formula $CO(CH:CMe_2)_2$, isoacetophorone by the formula $CMe_2<\begin{smallmatrix}CH_2-CO\\CH_2\cdot CMe\end{smallmatrix}>CH$, and camphorone by one or other of the expressions $CMe_2:C<\begin{smallmatrix}CO\cdot CHMe\\CH_2\cdot CH_2\end{smallmatrix}$ and $CH_2:CMe\cdot CH<\begin{smallmatrix}CO\cdot CHMe\\CH_2\cdot CH_2\end{smallmatrix}$.

M. O. F.

Camphorone, Isophorone, and Mesitylic Oxide. By WILHELM KERP and FRIEDRICH MÜLLER (*Annalen*, 1897, **299**, 193—235. Compare Abstr., 1896, i, 447, and preceding abstract).—For reasons which are stated in the paper, the authors consider that isophorone is Δ^1-trimethyl-1 : 3 : 3-cyclohexenone-5 (compare Knoevenagel and C. Fischer, Abstr., 1897, i, 611); they admit, however, that its behaviour on oxidation is more in agreement with the formula ascribed to it (isoacetophorone) by Bredt and Rübel. It is not improbable that the ketone is really a mixture of both isomerides. The view which is ultimately taken of the constitution of xylitone, $C_{12}H_{18}O$, the product of the condensation of acetone (1 mol.) with isophorone, must of course depend on the structure of the latter.

Isophorone boils at 98—100° under a pressure of 16 mm. The *dibromide*, $C_9H_{14}Br_2O$, is an unstable oil, which readily loses hydrogen bromide in the desiccator.

Trimethyl-1 : 3 : 3-*cyclohexanone*-5-*sulphonic acid*,

$$CH_2<\begin{smallmatrix}CMe_2\cdot CH_2\\CO—CH_2\end{smallmatrix}>CMe\cdot SO_3H,$$

is obtained by the action of sulphurous acid on isophorone in aqueous suspension. The *sodium* salt separates from water and from alcohol in large crystals; the *barium* salt contains $2H_2O$.

Methylisobutylketosulphonic acid, $SO_3H\cdot CMe_2\cdot CH_2\cdot COMe$, has been obtained from mesitylic oxide and sulphurous acid by Pinner (Abstr., 1882, 941), in the form of a sodium salt. The *barium* salt crystallises in lustrous leaflets containing $2H_2O$, and the *silver* salt is very sensitive to light and heat. *Methylisobutylketoximesulphonic acid*, $NOH:C_6H_{11}\cdot SO_3H$, crystallises from absolute alcohol, and melts and decomposes at 185—190°. The *sodium* salt separates from alcohol in white needles and melts, evolving gas, at 218°; the *barium* salt crystallises from alcohol in leaflets, and contains $1H_2O$.

Trimethyl-1 : 3 : 3-*amido*-5-*cyclohexane* (*dihydroisophorylamine*),

$$CHMe<\begin{smallmatrix}CH_2——CMe_2\\CH_2\cdot CH(NH_2)\end{smallmatrix}>CH_2,$$

obtained from isophorone and ammonium formate, boils at 183—185°; the *hydrochloride* does not melt below 250°. The *oxalate* crystallises in white leaflets and melts at 221·5°; the *carbamide* melts at 125—125·5°.

Oxidation of isophorone with potassium permanganate yields unsymmetrical dimethylsuccinic acid, along with an *acid*, $C_8H_{12}O_4$, which crystallises from water in large, rhombic plates, and separates from benzene in stellate aggregates of prisms; it melts at 102—103°.

Metanitrobenzylideneisophorone, $C_9H_{12}O:CH\cdot C_6H_4\cdot NO_2$, is obtained by passing hydrogen chloride into a solution of metanitrobenzaldehyde in isophorone heated on the water bath; it crystallises from a mixture

of chloroform and light petroleum in small, sulphur-yellow needles and melts at 159—161°.

Xylitone, $C_{12}H_{18}O$, a viscous, yellowish oil, obtained as a bye-product in the preparation of isophorone, boils at 120—122° under a pressure of 14 mm., and has the odour of geranium oil. The *oxime* boils at 162—164° under a pressure of 14 mm. The ketone is readily oxidised by potassium permanganate, which gives rise to acetic and unsymmetrical dimethylsuccinic acids. *Benzylidenexylitone*,

$$C_{12}H_{16}O\colon CHPh,$$

boils at 230—240° under a pressure of 14 mm.

Dihydrocamphoronesulphonic acid, $C_9H_{15}O\cdot SO_3H$, obtained by the action of sulphurous acid on camphorone, crystallises from a mixture of ether and alcohol, and dissolves very readily in water; the *barium* salt contains $2H_2O$.

β-Camphorone, $C_9H_{14}O$, is obtained by the action of alkalis on dihydrocamphoronesulphonic acid; it boils at 79—80° under a pressure of 14 mm. The *oxime* crystallises from alcohol and melts at 82—82·5°. A mixture of β-camphorone and benzaldehyde, when treated with alcoholic sodium ethoxide, yields a *compound* which boils at 200—205° under a pressure of 14 mm. M. O. F.

Bitter Almond Water. By Paul Fromm (*Chem. Centr.*, 1897, i, 1101; from *Apoth. Zeit.*, 12, 254—257).—The so-called artificial bitter almond water contains hydrocyanic acid, benzaldehyde, benzaldehyde-cyanhydrin, water, and alcohol, whilst that obtained by distilling bitter almonds contains not only these compounds, but also small quantities of ammonia and of (amido?) substances which have a peculiar odour, and whose physiological action has not been investigated. The benzaldehyde-cyanhydrin does not distil over as such, but is formed in the distillate at first comparatively quickly, and then more slowly during about 8 days; after this time, however, combination ceases, although free benzaldehyde and free hydrocyanic acid are still present.

Analyses of samples of bitter almond water obtained from various firms are given, and show percentages of uncombined hydrogen cyanide varying from 6·41 to 17·64 of the total present. The author determines the quantity of benzaldehyde volumetrically by a modification of Denner's method of forming the hydrazone and then decomposing it with iodine (V. Meyer), which is said to give fairly concordant results, although those quoted are constantly 20 per cent. too low. In order to distinguish the artificial from the real product, advantage is taken of the fact that, whilst the latter is practically free from chlorine, the former contains small quantities derived from the commercial benzaldehyde used. Ten c.c. of the water are treated with 20 c.c. of hydrogen peroxide solution free from hydrochloric acid, and then warmed with 2—3 grams of pure sodium hydroxide until the bitter almond odour disappears; the residue obtained by evaporating and gently igniting is then tested with silver nitrate. E. W. W.

Action of Nitric Acid on Desmotroposantonin. By Americo Andreocci (*Real. Accad. Linc.*, 1896, [v], 5, ii, 309—313).—The production of desmotroposantonin by the action of hydrogen chloride or bromide on santonin may be explained on the assumption that the

halogen hydride first attaches itself to the ketonic group, and is then eliminated with formation of the hydroxy-compound. This view is supported by the formation of an additive compound of santonin and nitric acid; santonin is dissolved in nitric acid of sp. gr. = 1·40, and the solution allowed to evaporate spontaneously, or it is diluted with a little water, when large crystals separate of a *compound* to which the author assigns the constitution

$$\begin{array}{l} \quad CH_2{-}{-}CMe{:}C{\cdot}CH_2{\cdot}CH{-}{-}{-}{-}{-}O \\ OH{\cdot}C(NO_2){\cdot}CMe{:}C{\cdot}CH_2{\cdot}CH{\cdot}CHMe{\cdot}CO \end{array}.$$

This nitrate decomposes at 120—140° with formation of some santonin, and is quantitatively dissociated into nitric acid and santonin by cold water.

Desmotroposantonin yields a *mononitro*-derivative of the constitution $\begin{array}{l} NO_2{\cdot}C{\cdot}CMe{:}C{\cdot}CH_2{\cdot}CH{-}{-}{-}{-}O \\ OH{\cdot}C{\cdot}CMe{:}C{\cdot}CH_2{\cdot}CH{\cdot}CHMe{\cdot}CO, \end{array}$ with cooled dilute nitric acid; this crystallises in beautiful, yellow prisms, melting with decomposition at 191°, and gives a red *sodio*-derivative. On treatment with concentrated nitric acid at the ordinary temperature, desmotroposantonin yields a small proportion of a *nitroxy*-derivative which probably contains the group $\begin{array}{l} \qquad\quad CO{\cdot}CMe{:}C{-} \\ NO_2{\cdot}O{\cdot}CH{\cdot}CMe{:}C{-} \end{array}$; it crystallises in colourless prisms melting and decomposing at 240°, and is accompanied by a larger proportion of a *substance* which crystallises in yellow needles; the latter melts with decomposition at 145° and gives an orange-coloured *phenylhydrazone*. W. J. P.

Oxidation Products of Santonic Acid. By LUIGI FRANCESCONI (*Real. Accad. Linc.*, 1896, [v], 5, ii, 214—222).—Santonic acid, on oxidation with cold potassium permanganate (Abstr., 1894, i, 204), gives a tetracarboxylic acid, $C_{13}H_{18}O_8$ (α) which melts at 176°, being converted into the *monanhydride*, melting at 193°, of an isomeric acid (β). The α-acid has the specific rotation $[\alpha]_D = +28·56°$, yields a liquid *tetramethylic* salt having $[\alpha]_D = +56·02°$, and with acetic anhydride gives a *dianhydride* melting at 134°. The dianhydride takes up water yielding the α-acid, whilst the monanhydride combines with water to give the β-acid; the α-acid crystallises unaltered from boiling hydrochloric acid, but yields the β-acid when heated with hydrochloric acid at 180°. The β-acid, which is not altered by heating with hydrochloric acid at 180°, has the specific rotation $[\alpha]_D = +29·16°$, and yields an inactive *tetramethylic* salt melting at 101°. Neither acid combines with hydroxylamine, phenylhydrazine, or bromine, nor decolorises permanganate. The author concludes that the α-acid is the *cis*-compound of the constitution,

$$\begin{array}{l} COOH{\cdot}CMe{\cdot}CH{\cdot}CH_2{\cdot}COOH \\ COOH{\cdot}CMe{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \end{array},$$

whilst the β-acid is probably the *trans*-isomeride.

The α-acid, when heated with soda at 250—260°, gives hydrogen, carbonic anhydride, acetic acid, and a tribasic acid of the composition $C_{10}H_{16}O_6$, which is a mixture of a racemic inactive *acid* melting at 125° with a dextrorotatory *isomeride* of lower melting point. These

acids do not combine with hydroxylamine, phenylhydrazine, or bromine, and do not decolorise cold permanganate; the constitutions

$$COOH\cdot CHMe\cdot CH(CH_2\cdot CH_2\cdot COOH)_2$$

and $COOH\cdot CHMe\cdot CH(CH_2\cdot COOH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$ are assigned to the racemic and active acids respectively.

On heating the α-acid with soda at 380—400°, an oil of mint-like odour distils which consists of a ketone, $C_8H_{14}O$, boiling at 169—171°; as it is inactive, it is probably a *ketoethylhexamethylene* of the constitution, $CHEt{<}{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}CO$, derived from the racemic tribasic acid, $C_{10}H_{16}O_6$. On heating with red phosphorus and hydriodic acid, it yields a *hydrocarbon*, C_8H_{16}, of pleasant aromatic odour, boiling at 134°, which absorbs bromine with liberation of hydrogen bromide; it is probably an ethylhexamethylene.

The α-acid, $C_{13}H_{18}O_8$, is converted at 260—280° into the *anhydride*, $C_{12}H_{14}O_4$, of a dibasic ketonic acid; the *acid*, $C_{12}H_{16}O_5$, melts at 213—216° yielding the anhydride, and after crystallisation from water has the specific rotation $[\alpha]_D = -128{\cdot}1°$, whilst the crystals deposited from hydrochloric acid solution give the value $[\alpha]_D = -117{\cdot}7°$. The *dimethylic* salt melts at 92—93°; that prepared from methylic alcohol and hydrogen chloride has the specific rotation $[\alpha]_D = -106{\cdot}6°$, whilst a sample made from the silver salt and methylic iodide gave the value $[\alpha]_D = -111{\cdot}4°$. The *monomethylic* salt crystallises with $\frac{1}{2}H_2O$, and has the specific rotation $[\alpha]_D = -94{\cdot}5°$; it loses its water at 90°, and yields an *anhydride* melting at 135° on further heating. The dimethylic salt gives an *oxime* having the specific rotation $[\alpha]_D = +25{\cdot}62°$; the acid yields an *oxime* melting at 188°, and an *anhydride*, $C_{12}H_{14}O_4$, melting at 196°. Since the ketonic acid, $C_{12}H_{16}O_5$, is a derivative of the monanhydride of the β-tribasic acid, several constitutions are possible for it. W. J. P.

Chrysotoxin. By C. JACOBY (*Chem. Centr.*, 1897, i, 483; from *Pharm. Centr. H.*, **38**, 58).—Spasmotin or sphacelotoxin is not a homogeneous compound. Three substances, which possess similar therapeutic properties, were obtained from ergot, namely, *sphacelotoxin*, *secalintoxin* (a compound of sphacelotoxin with the inactive secalin), and chrysotoxin (a compound of sphacelotoxin with the inactive *ergochrysin*, $C_{21}H_{22}O_9$), identical with spasmotin. Chrysotoxin is pharmacologically as valuable as ergot, keeps unchanged for years, and in the form of its very soluble sodium compound is especially suitable for injecting. E. W. W.

Sphacelotoxin, the Active Principle of Ergot. By C. JACOBY (*Chem. Centr.*, 1897, i, 1059—1060; from *Arch. expt. Path. Pharm.*, **39**, 85—143. Compare preceding abstract).—*Chrysotoxin*, $C_{21}H_{22}O_9$, which possesses the active properties of ergot of rye, is precipitated from the ethereal extract by light petroleum, and after repeatedly dissolving and precipitating, is obtained as a yellow, tasteless, and odourless powder. It crystallises in needles from a saturated solution in ether; it is easily soluble in most organic solvents, but is insoluble in light petroleum, water, and dilute acids. It is very slightly soluble in alkalis and ammonia, and since it is precipitated from such solutions by carbonic anhydride, its composition is probably more analogous to that

of a phenol than to that of an acid. These alkaline solutions undergo gradual decomposition, and after keeping some time are no longer precipitated by carbonic anhydride or acetic acid, but with hydrochloric acid yield a red precipitate of the inactive ergochrysinic acid.

Secalintoxin, $C_{13}H_{24}N_2O_2$, which has a physiological action similar to that of chrysotoxin but quite unlike that of Kobert's cornutin, is obtained from the ethereal extract by shaking it with acetic acid and precipitating the acid extract with sodium carbonate. It is very easily soluble in alcohol, ethylic acetate, benzene, and chloroform, slightly so in ether, very slightly in water, and insoluble in light petroleum. It is only slightly soluble in alkalis, and cannot be precipitated from such solutions, but dissolves easily in acids. The oxalate may be prepared by precipitating its ethereal solution with an alcoholic solution of oxalic acid.

Ergochrysin is obtained as an inactive, yellow substance by repeatedly dissolving chrysotoxin in glacial acetic acid and precipitating with water.

Secalin, $C_{29}H_{55}N_6O_{14}$, which is prepared by adding light petroleum to the ethereal solution of secalintoxin, is inactive, and crystallises in needles; it dissolves in a dilute solution of ammonia or sodium hydroxide. With alcohol and hydrochloric acid, it gives an intense violet coloration.

Chrysotoxin and secalintoxin owe their active properties to sphacelotoxin, which was obtained as a tar, and contains no nitrogen. It is converted into the inactive ergochrysin by the action of alkalis dissolved in alcohol. Sphacelotoxin probably occurs in these substances in a state of combination. E. W. W.

A New Reaction of, and a New Substance obtained from, Gambier Catechu. By KARL DIETERICH (*Chem. Centr.*, 1897, i, 245; from *Pharm. Centr.-H.*, **37**, 855—860).—Two extracts of catechu are known in trade, the one, the real Pegu catechu, is obtained from the sapwood of *Acacia Catechu*, the other, Gambier catechu, obtained from *Uncaria Gambier*. The author finds that the latter furnishes the following characteristic reaction. When it is hydrolysed with a cold aqueous or alcoholic solution of potassium hydroxide and the alkaline solution shaken with light petroleum of sp. gr. = 0·7, the latter acquires a fine, green fluorescence; the substance dissolved can be obtained as a brittle, resinous mass which is insoluble in water and contains no nitrogen. A 2 per cent. solution of Gambier catechu in alcohol, when boiled for 10 minutes with dilute hydrochloric acid, gives a blood-red coloration; on the other hand, the red colour of solution of Pegu catechu almost entirely disappears on boiling with hydrochloric acid. Both kinds give green colorations with ferric chloride in alcoholic solution, but in the case of Pegu catechu the solution rapidly becomes brown, and gives a dark-brown precipitate which turns bluish-violet with alkalis. With ferrous salts, solutions of Gambier catechu give a green and Pegu catechu a grey coloration. When alcoholic potash solution is added to a dilute solution of Pegu catechu in alcohol, a violet precipitate is formed; Gambier catechu gives a yellowish-white precipitate. Gambier catechu is partially soluble in alcohol, and forms

a clear solution, whilst Pegu catechu is sparingly soluble and forms a turbid solution. E. W. W.

Pyridine Periodides. By P. F. TROWBRIDGE (*Journ. Amer. Chem. Soc.*, 1897, 19, 322—331. Compare Abstr., 1896, 186, 316).—Pyridine methyl pentiodide, obtained when pyridine is added to an alcoholic solution of iodine containing methylic iodide, melts at 44·5°. *Pyridine methyl heptiodide* produced by the action of excess of iodine on pyridine methiodide in alcoholic solution, crystallises from dilute alcohol in slender, green needles melting at 26°; no higher periodide has been prepared.

Pyridine ethyl pentiodide forms black crystals melting at 83°, but as a compound of this nature should melt below 44°, the author thinks it probable that it may be ethylpyridine hydriodide tetriodide,

$$C_5NH_4Et,HI,I_4.$$

Pyridine hydriodide, $C_5NH_5,HI + H_2O$, forms white, needle-shaped crystals melting at 268° with some decomposition; if kept, it becomes brown and gives off pyridine. The *hydriodide*, C_5NH_5,HI, is made by adding freshly distilled hydriodic acid to well-cooled, pure pyridine; the white crystals, melting at 100°, can be recrystallised from water without taking up H_2O.

Pyridine hydrogen di-iodide prepared by treating pyridine with hydriodic acid containing iodine, or by adding an alcoholic solution of iodine to pure pyridine hydriodide, crystallises in dark brown needles melting at 188—191°; the *pentiodide* forms dark brownish-black crystals melting at 78—82°, and the *heptiodide* lustrous, green scales melting at 63—64°. The author has been unable to prepare the corresponding tri-iodide.

Pyridine ethyl tri-iodide forms bluish-black, thin, rhomboidal overlapping plates melting at 51°.

For the determination of the molecular weight of these substances, the freezing point method was employed, using phenol as solvent. The structure of these compounds is discussed, and the possibility of an iodine atom exerting an even valency is suggested. A. W. C.

Direct Introduction of Hydroxyl into 3-Hydroxypyridine. By RICHARD KUDERNATSCH (*Monatsh.*, 1897, 18, 613—628).—When 3-hydroxypyridine (20 grams) is fused with potassium hydroxide (250 grams), a *dihydroxypyridine*, $C_5NH_3(OH)_2$, is formed; to purify it, the crude product is converted into its acetyl compound, which is then hydrolysed by boiling water; on cooling, pure dihydroxypyridine crystallises out in colourless needles or white plates, which darken on exposure to the air. It is easily soluble in hot water, alcohol, and ethylic acetate, but almost insoluble in ether, benzene, chloroform, and petroleum. On being heated, it darkens at 220°, and melts and decomposes at 248° (uncorr.). Its solutions are coloured an intense blue by ferric chloride. The *hydrochloride*, $C_5H_5NO_2,HCl + H_2O$, crystallises in colourless plates, and melts at 106° (uncorr.), the anhydrous salt melting at 154° (uncorr.). The *platinochloride*,

$$(C_5H_5NO_2)_2,H_2PtCl_6 + H_2O,$$

crystallises in orange-red plates, and decomposes, without melting, at 130° (uncorr.); both these salts are easily decomposed by water. The

monacetyl derivative crystallises in colourless needles, melts at 156° (uncorr.), and is hydrolysed when boiled with water or alcohol.

It appears probable, from the mode of formation (compare Diamant, Abstr., 1896, i, 105), and from its failing to give condensation products with phthalic anhydride, or with orthophenylenediamine, that the new derivative is a 2 : 5-dihydroxypyridine. A *pyridoquinone* (*diketodihydropyridine*), $C_5H_3NO_2$, is obtained when it is oxidised with manganic hydroxide in sulphuric acid solution ; this is insoluble in all ordinary solvents, but separates from fused acetanilide as a microcrystalline, brownish-violet powder. It decomposes above 200° without melting, and is reduced by sodium amalgam, and probably also by sulphurous acid, to the dihydroxy-compound from which it was prepared ; it yields a crystalline *compound* with phenylhydrazine. W. A. D.

β-Acetoacetylpyridyl [3-Acetoacetylpyridine]. By ANDOR FERENCZY (*Monatsh.*, 1897, 18, 673—685).—*3-Acetoacetylpyridine*,

$$C_5NH_4\cdot CO\cdot CH_2Ac,$$

is prepared by adding an ethereal solution of ethylic nicotinate (1 mol.) and acetone (1 mol.) to sodium ethoxide, cooled so that the temperature does not rise above 40° ; it crystallises in soft, white needles, melts at 85° (uncorr.), and boils at 171° under a pressure of 15 mm. It is easily soluble in benzene, ether, alcohol, and acetone, but only sparingly so in water, and its aqueous and alcoholic solutions are coloured intensely red by ferric chloride. The *hydrochloride*, $C_9H_9NO_2,HCl$, crystallises in slender, slightly lustrous needles, and melts and decomposes at about 92° ; the *platinochloride*, $(C_9H_9NO_2)_2,H_2PtCl_6$, forms small, reddish-yellow, lustrous crystals, and melts, with decomposition, at 173—175° (uncorr.). Two *compounds* of the base with mercuric chloride are described ; the first, $C_9H_9NO_2,HCl,HgCl_2$, crystallises from dilute hydrochloric acid, and melts and decomposes at 123—125° (uncorr.) ; on dissolving this in alcohol, crystals of the second *compound*,

$$C_9H_9NO_2,HgCl_2,$$

melting and decomposing at 107—110° (uncorr.), are obtained.

The *sodium* derivative, $C_5NH_4\cdot CO\cdot CHNaAc$, of the diketone crystallises in slender, white needles. A *dioxime*, $C_9H_{11}N_3O_2$, is formed on adding hydroxylamine hydrochloride to 3-acetoacetylpyridine dissolved in dilute caustic soda ; this crystallises from alcohol, is easily soluble in water, and melts at 79° (uncorr.) ; with phenylhydrazine, the diketone yields an oily *compound*, which is probably a pyrazole, analogous to that obtained in a similar manner from 2-acetoacetylpyridine (Micko, Abstr., 1897, i, 95) ; with ethylic iodide it yields an additive *compound*, which crystallises in light yellow plates and melts at 198—199° (uncorr.).

3-Acetoacetylpyridine is decomposed by alkalis into acetone and nicotinic acid, and, on reduction with zinc dust and acetic acid, yields a *keto-alcohol* (probably $C_5NH_4\cdot CH(OH)\cdot CH_2Ac$), which melts at 115—117°. The *aurochloride*, $C_9H_{11}NO_2,HAuCl_4$ is a yellow, crystalline powder which melts at 143—145°.

By distilling 3-acetoacetylpyridine with zinc dust, the author obtained a colourless *oil*, which boiled at 210—220° ; its *aurochloride*,

$$C_8H_9NO,HAuCl_4,$$

crystallises in bright yellow needles. The paper closes with a comparison between the derivatives described, and the corresponding ones obtained by Micko (*loc. cit.*) from 2-acetoacetylpyridine. W. A. D.

Action of Ethylic Cyanacetate on Methyl Ethyl Ketone in Presence of Ammonia. By ERNESTO GRANDE (*Chem. Centr.*, 1897, i, 903; from *Atti R. Accad. Torino*, 32).—By treating methyl ethyl ketone with ethylic cyanacetate in presence of aqueous ammonia and evaporating, an *acid* is obtained which crystallises in leaflets and melts at 192—193°, and also its ammonium salt which does not melt at 260°; these compounds have not yet been completely examined. When ammonia is passed into a cooled mixture of the ketone and ethylic cyanacetate, hydrogen cyanide, ethane, and the ammonium salt of 3:5-dicyano-6-hydroxy-4-methyl-$\Delta^{3,6}$-dihydropyridone or dicyano-γ-methylglutaconimide are formed. The last substance is identical with that obtained by Quenda and by Pasquali (see following abstracts). The magnesium salt crystallises with $4\frac{1}{2}H_2O$, and the copper salt with $9H_2O$. E. W. W.

Action of Ammonia and Ethylic Cyanacetate on Ethylic Ethylideneacetoacetate and Acetaldehyde. By ENRICO QUENDA (*Chem. Centr.*, 1897, i, 903; from *Atti R. Accad. Torino*, 32).—From the product of the action of ammonia and ethylic cyanacetate on ethylic ethylideneacetoacetate, a substance which melts at 210—212°, of unknown composition first separates, then the ammonium salt of dicyanomethylglutaconimide (see preceding abstract) and finally small quantities of ethylic dihydrocollidinedicarboxylate. The last owes its formation to Hantzsch's reaction between ammonia and the acetoacetate, whilst the glutaconimide results from the action of the cyanacetate and ammonia on the acetaldehyde which is formed by the decomposition of the acetoacetate, for if acetaldehyde be used instead of ethylic acetoacetate the same glutaconimide is produced. *Dicyanomethylglutaconimide*, $\begin{matrix}OH\cdot C\text{—}CH(CN)\\ \parallel \qquad\qquad \\ N\cdot CO\cdot C(CN)\end{matrix}\!\!>\!CMe$, crystallises in lustrous leaflets, is very easily soluble in water and alcohol, gives a violet-blue coloration with ferric chloride, and contains $2\frac{1}{2}H_2O$, which it retains at 244°; the anhydrous salt melts at 250—252°. The *ammonium* salt crystallises with $2H_2O$, and the *barium* salt with $4H_2O$. E. W. W.

Action of Ethylic Cyanacetate and Ammonia on Fatty Ketones. By ADALBERTO PASQUALI (*Chem. Centr.*, 1897, i, 903—904; from *Atti R. Accad. Torino*, 32).—By the action of ammonia and ethylic cyanacetate on acetone, according to Guareschi, diacetonamine is first formed, and then a derivative of tetrahydropyridine, $NH\!<\!\begin{matrix}CMe_2\cdot CH_2\\ CO\cdot C(CN)\end{matrix}\!>\!CMe$. When higher homologues of acetone are used, different substances are obtained, according to whether the product is evaporated, or acidified with hydrochloric acid, but the ammonium salt of dicyanomethylglutaconimide (see preceding abstract) is invariably formed. This may result from the removal of a hydro-

carbon, RH, from an intermediate product, $\begin{matrix} C(ONH_4)\cdot CH(CN) \\ \| \\ N\cdot CO \text{——} CH(CN) \end{matrix}\!\!>\!CRMe$, and in the case of methyl propyl ketone, the product of the reaction when treated with mercury was found to yield propane. By the action of ammonia and ethylic cyanacetate on methyl hexyl ketone, a compound, $C_{11}H_{15}N_3O$, is formed, which crystallises in plates, melts at 152°, is slightly soluble in water and is decomposed into the ammonium salt of dicyanomethylglutaconimide and hydrogen cyanide by the action of aqueous ammonia; besides this, a substance, $C_3H_4N_2O$, which is slightly soluble in water, becomes brown at 300° without melting, and is not identical with cyanacetamide, is also produced. Methyl butyl ketone also yields the substance, $C_3H_4N_2O$, and a compound, $C_9H_{11}N_3O_2$, which melts at 177—178°, and when acted on by ammonia forms the ammonium salt of dicyanomethylglutaconimide. Methyl propyl ketone yields a compound, $C_8H_9N_3O$, which is also decomposed by ammonia with formation of the ammonium salt of dicyanomethylglutaconimide and hydrogen cyanide.

From acetone, a compound, $C_6H_5N_3O$, is obtained which crystallises in leaflets, melts at 213—214°, and is decomposed by ammonia, forming a substance, $C_8H_8N_4O_2$, which, however, does not yield dicyanomethylglutaconimide when treated with hydrochloric acid, but a compound which melts at 180—182°. E. W. W.

Derivatives of Ethylic Propionylpropionate. By LUIGI SABBATANI (*Chem. Centr.*, 1897, i, 904—905; from *Atti R. Accad. Torino*, 32.)—Ethylic propionylpropionate, obtained by the action of sodium on ethylic propionate, boils at 198°; on agitating this liquid with aqueous ammonia, the ethylic salt of an amido-acid separates and propionylpropionamide remains in solution. By the action of ethylic cyanacetate on a solution of the latter, a clear liquid is obtained, which after a few days deposits a white precipitate of the ammonium salt of 3-*cyano*-6-*hydroxy*-4-*ethyl*-5-*methyl*-$\Delta^{3,6}$-*dihydropyridone* or *methylcyanethylglutaconimide*, $\begin{matrix} C(ONH_4)\cdot CHMe \\ \| \\ N\cdot CO \text{——} C(CN) \end{matrix}\!\!>\!CEt$; this, on exposure to the air, becomes red. It dissolves in 381 parts of water, reddens blue litmus, decomposes carbonates, gives a blue coloration with ferric chloride and a red precipitate with copper sulphate, does not react with nitrites or with bromine, turns brown at 250°, and melts and decomposes at 261—262°. The ammonium, silver, sodium, barium, and copper salts were prepared and analysed.

On shaking ethylic propionylpropionate with methylamine, the ethylic salt of an amido-acid, probably of the composition

$$NH_2\cdot CEt\!:\!CMe\cdot COOEt,$$

separates and propionylpropionomethylamide, $COEt\cdot CHMe\cdot CO\cdot NHMe$, remains in solution. By the action of ethylic cyanacetate on the latter, a methylamine salt is obtained from which hydrochloric acid liberates 3-*cyano*-6-*hydroxy*-1 : 3-*dimethyl*-4-*ethyl*-$\Delta^{3,5}$-*dihydropyridone* or *methylcyanethylglutaconmethylimide*, $NMe<\begin{matrix} C(OH)\!:\!CMe \\ CO-C(CN) \end{matrix}>CEt$; this is a monobasic acid, slightly soluble in water. It melts and decomposes at 198°, gives a blue coloration and a white precipitate with ferric chloride, a

white precipitate with bromine, a yellow coloration when warmed with sodium nitrite, and is precipitated by silver nitrate but not by copper salts. E. W. W.

Synthesis of Pyridine Compounds and Hantzsch's Reaction. By ICILIO GUARESCHI (*Chem. Centr.*, 1897, i, 927—928; from *Atti R. Accad. Torino*, 32. Compare Abstr., 1897, i, 168—169).—In the reaction investigated by Quenda (see preceding abstracts), dicyanomethylglutaconimide is formed by the condensation of acetaldehyde (1 mol.), ethylic cyanacetate (2 mols.), and ammonia (1 mol.), with elimination of alcohol, water, and hydrogen. It has not yet been ascertained whether the hydrogen is liberated or takes part in secondary reactions. The formation of the substance which melts at 210—212° may be due to a similar reaction between ethylic acetoacetate, acetaldehyde and ammonia, in molecular proportion. Benzaldehyde, ethylic cyanacetate, ethylic acetoacetate, and ammonia react to form a compound which melts at 222—223°, and which may also result from a like reaction between these compounds in molecular proportion. The author proposes to ascertain whether, by a further extension of Hantzsch's reaction, aldehyde-ammonia, aldehyde, and ethylic cyanacetate may not form a substance of the formula $N{<}\begin{matrix}CH-CH_2\\CO\cdot C(CN)\end{matrix}{>}CMe$. From the fact that, by the action of ethylic cyanacetate on ketones of the type R·CO·Me in presence of ammonia (see Pasquali, preceding abstracts), dicyanomethylglutaconimide and a hydrocarbon are always formed, it is evident that the group COMe is eliminated, the residue forming a hydrocarbon. Intermediate products are obtained which, when decomposed by water, yield dicyanomethylglutaconimide and a hydrocarbon. E. W. W.

Alkoxides of 3-Hydroxyquinoline. By ADOLPH CLAUS and HANS HOWITZ (*J. pr. Chem.*, 1897, [ii], **56**, 438—444. Compare Abstr., 1896, i, 698).—3-Methoxyquinoline methiodide, already prepared by Skraup, can be obtained quite well from 3-hydroxyquinoline (1 mol.) by heating it with methylic iodide (rather more than 2 mols.) and potassium hydroxide (1 mol.); it melts and decomposes at 235—240°, and crystallises with $1H_2O$, as well as anhydrous. Treatment with silver chloride converts it into the *methochloride*, which decomposes at 234°, and crystallises with $1H_2O$. Both these salts, when heated with potash, yield a product which dissolves in ether forming a yellow solution, and remains, after evaporation of the ether, as an unstable, viscid liquid; this is probably a methylenequinolinium base (Abstr., 1892, 878). With silver oxide and water, they yield 3-methylquinolinium methohydroxide, which is insoluble in ether, and forms yellowish-red, unstable crystals; acids convert it into the corresponding metho-salts.

3-*Ethoxyquinoline methiodide* is obtained from 3-ethoxyquinoline and methylic iodide at 100°; it is yellow, decomposes at 195—197°, and crystallises with $1H_2O$. Treatment with silver chloride converts it into the *methochloride*, which decomposes above 200°, and crystallises with $1H_2O$. The *ethobromide* is obtained by using ethylic bromide, at 100°; it crystallises with $2H_2O$, and then melts at about 100°; when anhydrous, it decomposes at 210°. The *benzylochloride*, obtained with

benzylic chloride at 200° crystallises with $3H_2O$, and then melts at 96°; this, when heated with silver oxide and water, yields *both* the benzylidene and the benzylhydroxide base. C. F. B.

Synthesis of Naphthindole Derivatives. By OSCAR HINSBERG and A. SIMCOFF (*Ber.*, 1898, **31**, 250—254).—A small quantity of Cosiner's β-naphthylglycocine-β-naphthylamide,

$$C_{10}H_7 \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot C_{10}H_7$$

(Abstr., 1887, 605), is obtained when sodium naphthindolesulphonate is boiled with an excess of moderately dilute potassium hydroxide. If the sodium salt is distilled by itself, or, still better, with twice its weight of zinc dust in a stream of dry hydrogen at as low a temperature as possible, the chief product is *β-naphthindole*, $C_{10}H_6<^{NH}_{CH}>CH$, a considerable amount of an oily product being also formed. The indole forms large crystals melting at 39—40° and is readily soluble in most organic solvents. It yields a brownish-red, crystalline *picrate*, and with sodium nitrite and hydrochloric acid gives a brown precipitate. It is not identical with Schlieper's β-naphthindole (Abstr., 1887, 153). Isonitrosonaphthoxindole, which has been previously obtained by converting naphthindolesulphonic acid into naphthoxindole and then nitrosating, is more readily obtained as follows. A solution of potassium naphthindolesulphonate (1 gram) in 100 c.c. of hot water is cooled to 70° and then treated with acetic acid (10 c.c.) and a 10 per cent. solution of sodium nitrite (10 c.c.); the brownish-red precipitate of crude isonitrosonaphthoxindole, after being purified by recrystallisation from water, melts at about 230°. β-Naphthisatin is best obtained by boiling the isonitroso-compound (1 gram) with 20—30 c.c. of sulphuric acid (b. p. 130°) for $2\frac{1}{2}$—3 hours. After recrystallisation from alcohol, it melts at 252°.

Naphthindophenazine, $C_{10}H_6<^{NH \cdot C:N}_{\_\_\_\_ \, C:N}>C_6H_4$, is formed when orthophenylenediamine and β-naphthisatin are heated at 250° in an oil bath. The crude product is finely powdered, washed with water and alcohol, and then recrystallised from acetic acid; it forms pale yellow needles which melt above 300° and gives a deep violet coloration with sulphuric acid.

When β-naphthisatin is reduced with acetic acid and zinc dust, it yields *β-naphthodioxindole*, $C_{10}H_6<^{-NH-}_{CH(OH)}>CO$, which is precipitated when the hot acetic acid solution is poured into water. After recrystallisation from alcohol containing a small quantity of sulphurous anhydride in solution, it is obtained in the form of colourless, or slightly brown, crystals melting at 216°. It is readily oxidised by atmospheric oxygen to β-naphthisatin. J. J. S.

Action of Ethylic Oxalacetate on Guanidine and Derivatives of Carbamide. By R. MÜLLER (*J. pr. Chem.*, 1897, [ii], **56**, 475—506. Compare Abstr., 1897, i, 549, where *for* ethylic oxalate, dioxalguanidine, and dioxalcarbamide *read* ethylic oxalacetate, dioxal-

acetoguanidine, and dioxalacetocarbamide).—These substances are obtained by mixing ethylic oxalacetate with guanidine carbonate or carbamide, and a little acetic acid, heating the mixture to boiling, and then allowing it to remain for several days until crystallisation is complete. Ethylic dioxalacetoguanidine is decomposed by cold dilute hydrochloric acid into ethylic oxalacetate and guanidine; ethylic dioxalacetocarbamide is much more stable, and is not decomposed, even on boiling; alcoholic hydrochloric acid at 110° decomposes it completely, eliminating carbonic anhydride and ammonia. When nitrous anhydride is passed into a cooled solution of ethylic dioxalacetoguanidine, *ethylic dioxalacetonitrosoguanidine*,

$$NO\cdot N\colon C[N\colon C(COOEt)\cdot CH_2\cdot COOEt]_2,$$

melting and decomposing at 127—128°, is formed; ethylic dioxalacetocarbamide yields, first carbamide nitrate, and eventually ammonium nitrate. With neither ethylic dioxalacetoguanidine nor ethylic dioxalacetocarbamide does either ammonia, aniline, or sodium ethoxide yield any well-defined product; fuming nitric acid does act on them, however, yielding products that melt at 98·5° and 131° respectively.

Ethylic phenyluracilcarboxylate and *methyluracilcarboxylate*,

$$CO<\begin{matrix}NR\cdot C(COOEt)\\NH\text{———}CO\end{matrix}>CH \ [R = Ph,Me],$$

are obtained in the same manner as the unsubstituted uracilcarboxylate, starting from phenyl- and methyl-carbamide; they melt at 185° and 139·5° respectively. Ethylic uracilcarboxylate yields a *monacetyl* derivative, $CO<\begin{matrix}NAc\cdot C(COOEt)\\NH\text{———}CO\end{matrix}>CH$, melting at 139°; the phenyl- and methyl-uracilcarboxylates yield no such derivatives. With silver nitrate, ethylic uracilcarboxylate forms a *silver* salt, presumably $CO<\begin{matrix}NAg\cdot C(COOEt)\\NH\text{———}CO\end{matrix}>CH + H_2O$, but the phenyl and methyl derivatives form no such salts; this salt reacts with methylic iodide, but the product, curiously enough, melts at 112°, lower by 27° than the ethylic methyluracilcarboxylate described above. With alcoholic sodium ethoxide at the ordinary temperature, ethylic uracilcarboxylate forms a *disodium* salt, probably $CO<\begin{matrix}NH\cdot C(COONa)\\NNa\text{———}CO\end{matrix}>CH$, and this, with silver nitrate, yields the corresponding *disilver* salt; ethylic phenyl- and methyl-uracilcarboxylates, on the other hand, appear to yield products of the composition $CO<\begin{matrix}NR\cdot C(COOEt)\\NNa\text{———}CO\end{matrix}>CNa$. These products are decomposed by cold dilute hydrochloric acid, *β-phenyluramidacrylic acid*, $NH_2\cdot CO\cdot NPh\cdot CH\colon CH\cdot COOH$, melting and decomposing at 272°, and *β-methyluramidacrylic acid*, which is still unmelted at 300°, being formed. Ethylic uracilcarboxylate, in acetic acid solution, reacts with nitrous anhydride, yielding a product, $C_9H_8N_6O_8$, that melts at 240°, and forms compounds $C_9H_6Ag_2N_6O_8$ and $C_7Na_4N_6O_8$ when treated with silver nitrate and alcoholic sodium ethoxide respectively; with cold, red, fuming nitric acid, it yields the same product. It does not react with benzaldehyde, and therefore cannot contain a methylene group.

Neither triphenylguanidine nor diphenylcarbamide will condense

with ethylic oxalacetate; this makes it probable that in the condensation the water is eliminated from $\cdot NH_2$ and $\cdot CO\cdot$ groups of the carbamide and oxalacetate respectively, and not from $\cdot NH_2(\cdot NHR)$ and $\cdot C(OH)\colon$ (tautomeric form of the oxalacetate). In the condensation of carbamide with ethylic oxalacetate to ethylic uracilcarboxylate, the formation of ethylic β-uramidomaleate,

$$NH_2\cdot CO\cdot NH\cdot C(COOEt)\colon CH\cdot COOEt,$$

as an intermediate product must be assumed. C. F. B.

Reduction of 2:4-Pyrrodiazoles. By AMERICO ANDREOCCI and NICOLA CASTORO (*Real. Accad. Linc.*, 1896, [v], 5, ii, 343—346).—On reducing 1-phenyl-2:4-pyrrodiazole, $\begin{matrix} CH\colon N \\ \vert \\ N\colon CH \end{matrix}\!\!>NPh$, in absolute alcohol with sodium, aniline, methylamine, ammonia, a little hydrogen cyanide, and a small proportion of a pyrrodiazoline are produced. The investigation is being continued. W. J. P.

Action of the Phosphorus Chlorides on Oxygenated Derivatives of 2:4-Pyrrodiazoles. By AMERICO ANDREOCCI (*Real. Accad. Linc.*, 1897, [v], 6, i, 114—120 and 217—235).—1-Phenyl-3-methylpyrrodiazolone, $\begin{matrix} CMe\colon N \\ \vert \\ NH\cdot CO \end{matrix}\!\!>NPh$, is converted by phosphorus pentachloride at 150° into a mixture of two isomeric *monochloro*-derivatives, $C_9H_8N_3OCl$, which crystallise, one in thin needles melting at 247°, and the other in prisms melting at 163°; at lower temperatures, phosphoric anhydride, or a mixture of phosphorus trichloride, and pentachloride, converts the diazolone into a condensation *product*, $C_{18}H_{16}N_6O$, which crystallises in large prisms melting at 140°. A similar *anhydride*, $C_{16}H_{12}N_6O$, is obtained by treating 1-phenyl-5-pyrrodiazolone with phosphoric anhydride or a mixture of the two chlorides; it crystallises in needles melting at 162°, and both anhydrides are insoluble in alkalis; the two isomeric chloro-derivatives melting at 247° and 163° are *chlorophenylmethylpyrrodiazolones* of the constitution $\begin{matrix} CMe\colon N \\ \vert \\ NH\cdot CO \end{matrix}\!\!>N\cdot C_6H_4Cl$, and when oxidised with alkaline permanganate yield isomeric *chlorophenylpyrrodiazolonecarboxylic acids*, of the constitution

$$\begin{matrix} COOH\cdot C\!=\!=\!N \\ \qquad\vert \\ \qquad NH\cdot CO \end{matrix}\!\!>N\cdot C_6H_4Cl;$$

that from the substance melting at 247° melts at 130—200°, and decomposes, yielding a *substance* melting at 257°, whilst the acid from the compound melting at 163° melts and decomposes at 150—155°, yielding a *substance* melting at 152°. These products are *chlorophenylpyrrodiazolones* of the constitution $\begin{matrix} CH\!=\!N \\ \vert \\ NH\cdot CO \end{matrix}\!\!>N\cdot C_6H_4Cl$, and the isomeride melting at 257° is also obtained by treating the phenylpyrrodiazolone with phosphorus pentachloride.

1-Phenyl-5-pyrrodiazolone, when treated with a mixture of phosphorus pentachloride and oxychloride, yields the following compounds, namely, 1-*chlorophenyl*-5-*chloropyrrodiazole*, $\begin{matrix} C\colon HN \\ \vert \\ N\colon CCl \end{matrix}\!\!>N\cdot C_6H_4Cl$, which

crystallises in laminæ melting at 70°; 1-*phenyl-5-chloropyrrodiazole*, which crystallises in large prisms melting at 54°; and 1-*phenyl-pyrrodiazole*, $\genfrac{}{}{0pt}{}{\text{CH:N}}{\text{N:CH}}\!>\!\text{NPh}$, which melts at 47° and boils at 266°; this is also obtained by the action of phosphorus pentasulphide on 1-phenyl-5-pyrrodiazolone, or on 1-phenyl-3-oxypyrrodiazole. A *compound* which crystallises in thin, transparent laminæ melting at 133°, and seems to have the composition of a chlorophenylpyrrodiazole and an *anhydride* of the composition $C_{16}H_{11}ClN_6O$, which crystallises in thin needles, are also obtained.

The following compounds have been prepared in like manner from 1-phenyl-3-methylpyrrodiazolone. 1-*Chlorophenyl-3-methyl-5-pyrrodiazole*, $\genfrac{}{}{0pt}{}{\text{CMe:N}}{\text{N}=\text{CCl}}\!>\!\text{N}\cdot C_6H_4Cl$, which crystallises in long, transparent needles melting at 95°; 1-*phenyl-3-methyl-5-pyrrodiazole*, which crystallises in large prisms melting at 84°, and a *substance* which crystallises in long needles melting at 123° and has the composition of a 1-chlorophenyl-3-methylpyrrodiazole. A brown, viscous residue not volatile with steam is also obtained.

The action of a mixture of phosphorus pentoxide and oxychloride on phenylurazole yields a *phenyldichloropyrrodiazole*, which crystallises in small prisms melting at 94°, and probably has the constitution $\genfrac{}{}{0pt}{}{\text{CCl:N}}{\text{N:CCl}}\!>\!\text{NPh}$.

Phenylpyrrodiazolone, when heated with phosphorus oxychloride in a closed tube at 180°, yields the 1-phenyl-5-chloropyrrodiazole melting at 54°, and an *anhydride* of the composition $C_{16}H_{12}N_6O$, which melts at 162°. The same two substances and the 1-phenylpyrrodiazole melting at 47° are obtained by heating the phenylpyrrodiazolone with phosphorus trichloride in a closed tube at 180°.

The 1-phenyl-3-oxypyrrodiazole, when heated with phosphorus oxychloride at 200° yields 1-phenyl-3-chloropyrrodiazole, C_2N_3PhHCl, which melts at 76° and boils at 299°. W. J. P.

1-Phenyl-3-methylpyrrol-2:4-diazole Ethiodide and Ethobromide. By Americo Andreocci (*Real. Accad. Linc.*, 1897, [v], 6, i, 293—295).—1-Phenyl-3-methylpyrrol-2 : 4-diazole ethiodide,

C_2N_3HPhMe,EtI,

prepared by heating the diazole with ethylic iodide at 100—120° for several hours, crystallises in hard prisms melting at 181—182°, and is very soluble in water. The corresponding *ethobromide* crystallises in large prisms melting at 222—224°, and is also very soluble in water.

W. J. P.

Constitution of the Pyrroldiazolones. By Americo Andreocci (*Real. Accad. Linc.*, 1897, [v], 6, i, 378—386).—This paper is of theoretical importance only, and contains no new experimental results.

W. J. P.

Caffeine Compound in Kola. By James W. T. Knox and Albert B. Prescott (*J. Amer. Chem. Soc.*, 1897, 19, 63—90).—When kola seed is cut or bruised, chemical action at once takes place,

as is seen by the change in colour from pink to reddish-brown; that this is due to the action of a diastatic ferment seems probable, for no colour is developed when the freshly-cut seed is placed in boiling water. Cold does not impair the potency of the ferment, but seems to preserve it.

The method of Dohme and Engelhardt (*Amer. Drugg.*, 1896, 12) for the assay of kola only gives about one-half of the total caffeine, and the authors recommend the following process. To the measured caffeine solution acidified with hydrochloric acid, a definite volume of Wagner's reagent is added in excess, and after allowing the precipitate to settle, the liquid is filtered through asbestos. The excess of iodine is then titrated with decinormal thiosulphate solution, and from this the amount of Wagner's solution used up can be calculated, 1 c.c. corresponding with 0·00485 gram of anhydrous caffeine.

Hydrolysis with dilute acids is unsuitable for the complete recovery of the alkaloids of kola from their natural combination (kolanin), but if freshly precipitated lead hydroxide is used, the whole of the caffeine is liberated; this affords a trustworthy method for the determination of the combined alkaloids in kola. This action of kolanin with lead hydroxide indicates that it is of a tannin-like character, for there is reason to believe that the glucose obtained by the decomposition of the so-called glucoside (kolanin) with mineral acids exists primarily in combination with a tannin-like substance; the liberation of glucose is, therefore, not necessarily simultaneous with that of caffeine or a consequence of it. In all probability, kolanin is a combination of caffeine and theobromine with a glucoside-tannin. When an aqueous infusion of kola is poured into a 10 per cent. solution of caffeine acidified with hydrochloric acid, a precipitate is formed, and this "caffeine kolatannate" is identical in appearance and properties with kolanin, and differs but slightly from it in composition.

When kolanin is treated with diastase at 50—53°, caffeine is precipitated, but from a control experiment it appears that precipitation is due rather to the effect of water and heat than to the diastase, and the liberation of caffeine by the kola ferment itself is to be attributed to the same cause, for if the kola be sterilised, thus checking the formation of the coloured compound (kola red), the amount of alkaloid liberated is not diminished; caffeine and kola red are not therefore joint products of the one hydrolysis of a glucoside, as concluded by previous investigators.

A slight modification of Kunze's method (Abstr., 1894, ii, 168) for the estimation of theobromine in presence of caffeine gave very satisfactory results.

The melting point of the mixed free alkaloids and of the combined alkaloids of kola is the same, 225—227°, corresponding fairly well with that of pure caffeine.

The free tannin of kola is a light red to red-brown substance having a faintly acid and astringent taste and behaving like other tannins with iron salts, gelatin, and alkaloids. It is a glucosidal compound, as on hydrolysis with dilute mineral acids it yields glucose and a dark brown substance insoluble in water and alcohol. The combined tannin agrees with the above in appearance and properties. A. W. C.

New Synthesis of Adenine and its Methyl Derivatives. By EMIL FISCHER (*Ber.*, 1898, **31**, 104—122. Compare this vol., i, 48).—2-Chloro-6-amido-8-oxypurine is converted by phosphorus oxychloride into a mass which contains a large amount of dichloradenine, although this substance has not been isolated from it. When the crude product is warmed with hydriodic acid, it readily yields adenine, identical in all respects with the natural product and with that previously obtained from trichloropurine.

Synthesis of the Methyladenines.—2 : 6-Dichloro-8-oxy-9-methylpurine is converted by alcoholic ammonia at 140—150° into 2-*chloro*-6-*amido*-8-*oxy*-9-*methylpurine*, $\begin{array}{l}\mathrm{N{:}C(NH_2){\cdot}C{\cdot}NH}\\ \mathrm{CCl{:}N{-}{-}{-}C{\cdot}NMe}\end{array}\!\!>\mathrm{CO}$, which crystallises in short, lustrous needles, decomposes above 360°, and yields crystalline salts with hydrochloric, nitric, and sulphuric acids. When this base is heated with phosphorus oxychloride, 2 : 8-*dichloro*-6-*amido*-9-*methylpurine*, $\begin{array}{l}\mathrm{N{:}C(NH_2){\cdot}C{-}{-}N}\\ \mathrm{CCl{:}N{-}{-}{-}CNMe}\end{array}\!\!>\mathrm{CCl}$, is formed, which crystallises in rhombohedral forms, melts at 270° (corr.), and yields crystalline salts with mineral acids. On reduction with hydriodic acid, it yields the 9-methyladenine melting at 308—310° (corr.), which has been previously described. The isomeric 7-methyladenine is obtained by a similar series of operations from 2 : 6-dichloro-8-oxy-7-methylpurine. 2-*Chloro*-6-*amido*-8-*oxy*-7-*methylpurine* crystallises with $1H_2O$ in elongated, lustrous plates, which decompose when heated, and are very sparingly soluble in water. The base yields salts both with acids and bases, the *sodium* salt crystallising in slender, flexible needles. 2 : 8-*Dichloro*-6-*amido*-7-*methylpurine* crystallises in long, slender, flexible needles, and, when heated, decomposes without melting. It is sparingly soluble in water, and readily yields salts with acids but not with bases. 7-*Methyladenine*, $\begin{array}{l}\mathrm{N{:}C(NH_2){\cdot}C{\cdot}NMe}\\ \mathrm{CH{:}N{-}{-}{-}C{-}{-}{-}N}\end{array}\!\!>\mathrm{CH}$, forms a neutral solution in water, from which it separates as a granular powder, melting at 351° (corr.), and partially subliming at a higher temperature. The *hydrochloride* crystallises in microscopic, rectangular tablets, the *nitrate* in fascicular groups of needles, and the *sulphate* in well-developed prisms. This new base can also be obtained from 2 : 6-dichloro-7-methylpurine, which is converted by ammonia into 2-*chloro*-6-*amido*-7-*methylpurine*, a compound which crystallises in slender needles, and melts at about 284° (corr.), evolving gas. When heated with fuming hydrochloric acid, this substance yields heteroxanthine, whilst with hydriodic acid, 7-methyladenine is formed.

The Methylhypoxanthines.—By the action of nitrous acid, the methyladenines are converted into the corresponding methylhypoxanthines, of which the 7-methyl derivative has already been described. 9-*Methylhypoxanthine*, $\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C{-}{-}{-}N}\\ \mathrm{CH{:}N{-}C{\cdot}NMe}\end{array}\!\!>\mathrm{CH}$, which is only sparingly soluble in water, crystallises in narrow plates, and melts and decomposes at about 390° (corr.). It yields salts both with acids and bases, and on methylation is converted into a crystalline product which is probably a *dimethyl-compound*, but has not been analysed. 2-Chloro-6-amido-

8-oxy-7-methylpurine is converted by hydrochloric acid at 130° into 6-*amido*-2 : 8-*dioxy-7-methylpurine*, $\begin{matrix} N\!:\!C(NH_2)\cdot C\cdot NMe \\ CO\cdot NH - C—NH \end{matrix}\!\!>\!CO$, which crystallises with $1H_2O$ in microscopic plates, is very sparingly soluble in water, and decomposes above 320°. It gives the murexide reaction, but does not yield guanidine on oxidation with hydrochloric acid and sodium chlorate. The *hydrochloride* crystallises in prisms or slender needles, the *sulphate* in spherical aggregates, and the *sodium* salt in very slender, flexible needles. Dichloro-7-methylpurine is converted by aqueous ammonia into 2 : 6-*diamido-7-methylpurine*,

$$\begin{matrix} N\!:\!C(NH_2)\cdot C\cdot NMe \\ C(NH_2)\!:\!N\cdot C——N \end{matrix}\!\!>\!CH,$$

crystallising in long, slender needles, which melt and decompose at about 390° (corr.).

2-*Chloro*-6-*methylamido*-7-*methylpurine*, obtained by the action of methylamine on the dichlorinated base, crystallises with $2H_2O$ in lustrous plates, melts at 269° (corr.), and decomposes at a higher temperature. The *hydrochloride, nitrate, sulphate, aurochloride* and *platinochloride* are all crystalline, the last-named being only very sparingly soluble in water. Hydrazine acts on the dichloro-base in a somewhat similar manner to methylamine, but also forms complicated products. *Chloro-7-methylhydrazidopurine*, $C_6H_4N_4Cl\cdot NH\cdot NH_2$, crystallises in bundles of slender needles, and decomposes when heated. The base readily reduces platinic chloride and Fehling's solution, its constitution as a primary hydrazine being thus established. The salts with acids are all crystalline, the sparingly soluble *picrate* melting at 160—162°. *Hydrazomethylchloropurine*, $C_6H_4N_4Cl\cdot NH\cdot NH\cdot C_6H_4N_4Cl$, which is formed along with the foregoing compound, crystallises with $1H_2O$, and decomposes very readily when heated. It dissolves in both bases and acids, forming crystalline salts with the latter. A. H.

A Product of Hydrolysis from Arginine. By ERNST SCHULZE and ERNST WINTERSTEIN (*Ber.*, 1897, **30**, 2879—2882).—It has been already shown by Schulze and Likiernik (Abstr., 1891, 1521) that carbamide is produced by the hydrolysis of arginine with baryta. The authors have identified the remaining product as ornithin, described by Jaffé (Abstr., 1878, 584). Regarding this substance as diamidovaleric acid, they ascribe to arginine the constitution

$$NH\!:\!C(NH_2)\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH.$$

M. O. F.

Non-nitrogenous Decomposition Products of Morphine. By EDUARD VONGERICHTEN (*Ber.*, 1898, **31**, 51—56. Compare this vol., i, 98).—*Acetylmethylmorpholquinone*, $C_{17}H_{12}O_5$, is obtained by oxidising acetylmethylmorphol in glacial acetic acid solution with chromic acid; it crystallises from glacial acetic acid in lustrous, yellow needles, and melts at 205—207°. The solution in concentrated sulphuric acid is bluish-red, and a greenish-blue liquid is formed on treating the quinone with sodium hydroxide dissolved in methylic alcohol. It undergoes Laubenheimer's condensation when treated with toluene and glacial acetic and sulphuric acids. The production

of the quinone is analogous to the formation of acetylthebaolquinone (Freund, Abstr., 1897, i, 497). The *azine*, $C_{24}H_{18}N_2O_3$, is obtained from the quinone and orthotolylenediamine, and melts at 212°; the solution in concentrated sulphuric acid is deep greenish-blue, becoming bluish-red on dilution.

Attempts to improve the method of preparing morphenol methylic ether have led to the observation that this compound is derived from the methohydroxide of β-methylmorphimethine rather than from the α-derivative.

Oxidation of acetylmorphenol (m. p. 140°) yields an orthodiketone having phenolic properties; the compound is a derivative of phenanthraquinone. M. O. F.

Euquinine. By CARL VON NOORDEN (*Chem. Centr.*, 1897, i, 182, from *Centr. f. inn. Med.*, **17**, 1225).—*Euquinine* (*quinine ethylic carbonate*, $C_{20}H_{23}N_2O\cdot O\cdot COOEt$), is obtained by the action of ethylic chlorocarbonate on quinine. It crystallises in white needles, melting at 95°, has an alkaline reaction, is nearly tasteless, and forms crystallisable salts with acids. Like quinine, it shows a strong blue fluorescence when dissolved in sulphuric or nitric acid. It is recommended as a medicament in place of quinine, 1·5 to 2 grams of euquinine being equivalent to 1 gram of quinine salts. W. D. H.

Derivatives of Tropine. By A. VAN SON (*Arch. Pharm.*, 1897, **235**, 685—693).—*Tropinebetaine chloride*, $C_8H_{15}ONCl\cdot CH_2\cdot COOH$, is obtained by heating together tropine and monochloracetic acid; it forms an *aurochloride* crystallising from hot water in beautiful, feathery needles containing $1H_2O$ and melting at 223—224°, and a *platinochloride* separating from water in groups of prismatic crystals containing $2H_2O$ and melting at 227°. *Tropinecholine chloride*, prepared by the interaction of ethylenechlorhydrin and tropine, forms an *aurochloride* crystallising in long needles melting at 216°, and a *platinochloride* melting at 216—217°. *Tropinethylene bromide*, obtained from tropine and ethylenic dibromide, crystallises from alcohol in plates melting at 205—206°; when treated with silver chloride, one bromine atom is replaced by chlorine, and the resulting chlorobromide gives an *aurochloride* crystallising in plates and melting at 206—207°, and a *platinochloride* crystallising in yellowish-red plates or needles and melting at 215°. When the ethylenic bromide compound is treated with silver nitrate, it is converted into tropinecholine nitrate, as proved by the preparation of the aurochloride.

Tropineneurine, $C_8H_{15}ON(OH)\cdot CH\colon CH_2$, results from the action of freshly precipitated silver oxide on tropinethylene bromide. The *aurochloride* forms feathery needles melting at 223°, and the *platinochloride* crystallises in plates melting and slightly decomposing at 214°. On treatment with hydrogen bromide, it is converted into *tropineneurine bromide*, $C_8H_{15}ONBr\cdot CH\colon CH_2$, crystallising from alcohol in colourless needles, which blacken at 215° without melting. When treated with bromine in alcoholic solution, a *tribromide* is formed crystallising in colourless needles which decompose at 240° without melting. The *aurochloride* forms small needles melting at 214—215°. A. W. C.

Crystalline Physostigmine [Eserine]. By N. A. Orloff (*Chem. Centr.*, 1897, i, 1214; from *Pharm. Zeit. Russ.*, 36, 213—214).—By precipitating an aqueous solution of eserine sulphate with ammonia, allowing the precipitate to remain in the liquid for some time, and occasionally shaking, the alkaloid is obtained in a crystalline form. The author recommends the above as a general method of preparing crystalline alkaloids. E. W. W.

Pilocarpidine. By C. Emanuel Merck (*Chem. Centr.*, 1897, i, 476; from *Ber. ü. d. Jahr.*, 1896. Compare Petit and Polonowsky, Abstr., 1897, i, 581—582).—The author has been unable to confirm Harnack's statement that pure pilocarpidine may be obtained by means of the platinochloride. He finds also that the aurochloride is slightly soluble in water; this salt, $C_{10}H_{14}N_2O_2,HAuCl_4$, which melts at 125—128° and crystallises from glacial acetic acid in needles or prisms, is decomposed by hydrogen sulphide, yielding pilocarpidine hydrochloride, whose platinochloride, $(C_{10}H_{14}N_2O_2)_2,H_2PtCl_6 + 4H_2O$, melts at 100°; the anhydrous salt melts at 186—190°; Harnack states that the platinochloride decomposes at 130°. Pure pilocarpidine, which the author obtains from the aurochloride, is an alkaline syrup rather easily soluble in water, and has a specific rotatory power $[\alpha]_D = +72°$. It is decomposed by concentrated potassium hydroxide solution at 200° with liberation of dimethylamine. Hardy and Calmels state that they have obtained pilocarpine from pilocarpidine by means of methylic iodide, but the author has prepared pilocarpidine methiodide, converted it into the corresponding chloride, and obtained a platinochloride, $(C_{11}H_{16}N_2O_2)_2,H_2PtCl_6 + 4H_2O$, which softens at 175°, melts at 178°, and is not identical with pilocarpine hydrochloride.
E. W. W.

Carpaine. By J. J. L. van Rijn (*Chem. Centr.*, 1897, i, 985; from *Ned. Tijdschr. Pharm.*, 9, 47—63).—This is largely a repetition of the preliminary paper (compare Abstr., 1897, i, 647). Since methylcarpaine, $C_{14}H_{24}MeNO_2$, reacts with benzoic chloride, it probably contains a hydroxyl group. The author has also obtained a glucoside, which he names *carposide*, from papaya leaves; this crystallises in colourless needles, and is insoluble in ether but soluble in alcohol, and in water. Its aqueous solution reduces Fehling's solution only after boiling with dilute sulphuric acid. E. W. W.

Curara and Curara Alkaloids. By Rudolf Boehm (*Arch. Pharm.*, 1897, 235, 660—684).—The curara alkaloids may be divided into two classes. Those of the first series, like curine, are partly crystalline and partly amorphous, soluble in water with difficulty, and are precipitated from solutions by ammonia. They are soluble in ether and give, without exception, voluminous precipitates with metaphosphoric acid. The characteristic toxic effect of curara is shown very slightly or not at all by them. The members of the second series are, like curarine, amorphous, yellowish-red substances, easily soluble in water, but insoluble in ether, and cannot be precipitated from solutions of their salts by ammonium hydroxide or other alkalis. The halogen of their haloid

salts can only be completely removed by silver oxide and the alkaloids themselves show the most marked curara action.

Paracurara, or tube curara, is imported in bamboo tubes, and is the variety now usually met with in commerce. It is a dark brown mass impregnated with well-defined, yellowish coloured crystals of quercitol, often 2 cm. long. It contains 11—14 per cent. of water, and about 12 per cent. of ash, consisting for the most part of the carbonates, phosphates, and chlorides of potassium, calcium, and magnesium. Its toxic dose for rabbits is 0·005—0·01 gram per 1 kilo. body weight.

Its solutions are precipitated by concentrated nitric acid, and at the same time a red coloration is produced which is intensified on heating. Metaphosphoric acid causes a voluminous precipitate, as do also the alkalis, many metallic salts, and all alkaloid reagents.

Curine, $C_{18}H_{19}NO_3$ (Abstr., 1887, 1125) is contained in paracurara to the extent of 12—15 per cent. It may be isolated by extracting the raw material with water, precipitating the solution with aqueous ammonia, and extracting with dilute alcohol. It crystallises from benzene in colourless, glistening, four-sided prisms melting at 161°, from ethylic alcohol in crystals melting at 159—163°, and from methylic alcohol in crystals melting at 212°. In the first two cases, the crystals contain one molecule of the solvent, which may be eliminated by heating to 180° in a stream of hydrogen. Curine is soluble in dilute acids to form a colourless solution tasting at first sweet and then bitter; it also dissolves in concentrated alkalis, but is insoluble in water. When moistened with sulphovanadic acid, it dissolves, giving a black colour, but this soon becomes dark blue on the edges and then clear red. Metaphosphoric acid and all the alkaloidal reagents cause precipitation; ammoniacal silver nitrate solution is reduced, but no red colour is obtained with Millon's reagent.

The *platinochloride* is an amorphous, yellow powder insoluble in water and alcohol; the *methiodide* crystallises in slender, yellow needles melting at 252—253°; and the *methochloride* in colourless, rhombic plates. When the latter is acted on with silver oxide, the ammonium hydroxide *base* of quaternary methylcurine is obtained as an amorphous, yellowish-red powder.

Curine contains one methoxy-group; it cannot be benzoylated, but on treatment with methylic iodide and caustic potash the *methylic ether* of methylcurine is formed, as a non-crystalline substance, of which the platinochloride and aurochloride were analysed. When fused with potash, curine yields amino-bases and protocatechuic acid; and when distilled with soda lime or zinc dust, the principal product is trimethylamine, and also a substance giving the characteristic reactions for paraquinoneanisoil, showing the existence of a methoxyquinoline ring in curine.

Paracurarine (*tubocurarine*).—The filtrate, after extracting curine, contains quercitol and curarine, obtained by precipitation with mercuric chloride, &c. It is an amorphous, reddish-yellow substance, forming 9—11 per cent. of the raw curara. It is soluble in water and alcohol, forming a red solution with a green fluorescence, and is not identical with the previously known curarine isolated from calabash-curara. In its behaviour towards reagents, it resembles curine,

except that it is not precipitated by the alkali phosphates. The *platinochloride* and *hydriodide* are yellow, amorphous powders. Tubocurarine contains one methoxy-group, but, unlike curine, is not acted on by methylic iodide, and is therefore not a tertiary base.

Calabash-curara used to be the common variety, and is that to which earlier investigations, as a rule, refer, but it is now seldom met with; it was sent over in calabashes. It is a hard, dark brown substance, with a peculiar smell and a very bitter taste. Its watery solution, which is slightly acid, is coloured purple by concentrated sulphuric and nitric acids. The active principle is curarine, obtained together with minute quantities of a second alkaloid by precipitating an aqueous extract of the raw material with platinic chloride, decomposing with hydrogen sulphide, and extracting with a mixture of alcohol and chloroform. It forms hard, glistening, garnet-red laminæ, decomposing and giving off a smell of trimethylamine when heated at 150°. It is odourless, has an intensely bitter taste; and gives blue to violet colour reactions with concentrated sulphuric, nitric, or sulphovanadic acid. The *platinochloride* is an amorphous, strongly electrical powder, decomposing without melting when heated, and the *hydriodide* is the only compound which shows a tendency to crystallise.

A third variety of curara is sent over in small jars of unburnt clay; it is a dry, blackish-brown substance, and differs widely in the amount of active principle which it contains. The following substances have been extracted from it.

Protocurine, $C_{20}H_{23}NO_3$, crystallises from methylic alcohol in colourless, hair-like needles, which, on heating, turn brown at 160° and melt at 306° with decomposition. It gives no characteristic colour reactions. It yields crystalline salts possessing a bitter taste.

Protocuridine.—The free base is quite insoluble, but may be purified by boiling repeatedly with chloroform, when it is obtained in the form of hard, colourless, prismatic crystals melting at 274—276°; it is easily soluble in dilute acids, is precipitated by the usual alkaloidal reagents, but gives no characteristic colour reactions. The *sulphate* and *platinochloride* are crystalline substances.

Protocurarine is an amorphous, red powder, easily soluble in water and alcohol, and is more poisonous than the other curarines. Its salts are inactive. It gives characteristic colour reactions with sulphuric, nitric, and sulphovanadic acids, and reduces ammoniacal silver nitrate solution. A. W. C.

Enzymes. By WACLAW VON MORACZEWSKI (*Pflüger's Archiv.*, 1897, **69**, 32—75).—The question is investigated whether various enzymes (diastase, pepsin, fat-splitting enzymes, &c.) require calcium salts for their activity to be manifested in the same way as rennin does. It was found that no method of precipitating calcium salts inhibits the activity of these enzymes. The presence of calcium salts is favourable to their action, and in a few cases (ptyalin and diastase) the removal of calcium salts weakens their activity, but even this action is inconstant. W. D. H.

Influence of Heat on Diastatic Ferments. By ANGELO PUGLIESE (*Pflüger's Archiv.*, 1897, **69**, 115—131).—The research is

directed to the question whether diastase of vegetable origin is the same ferment as the diastatic enzymes of animals. Although it is regarded as probable that the enzymes are different, the problem is one which cannot yet be solved. Certainly, no difference in relationship to the temperature at which they are most active could be discovered.

W. D. H.

Chemical Nature of Diastase. By THOMAS B. OSBORNE (*Ber.*, 1898, **31**, 254—259. Compare Abstr., 1896, i, 398, and Wróblewski, this vol., i, 54).—The author considers that the reason why Wróblewski's diastase did not coagulate on warming to 50—60°, was on account of the small quantity of true diastase present. It has already been shown that dilute solutions of malt albumin and of other vegetable proteids do not coagulate. That Wróblewski's preparation was not so pure as the author's was proved by comparing the amount of maltose obtained by the aid of each. It is also stated in reply to Wróblewski that the author's preparations were quite free from the carbohydrate, araban.

J. J. S.

Betulase, an Enzyme contained in Betula Lenta. By AUGUST SCHNEEGANS (*Chem. Centr.*, 1897, i, 326; from *Journ. Pharm. d'Als.-Lorr.*, 1896, No. 17).—Gaultherin, the glucoside present in the bark of *Betula lenta*, on hydrolysis yields a carbohydrate and methylic salicylate, and by macerating the powdered bark of *Betula lenta* during four weeks with glycerol, the author has extracted an enzyme, *betulase*, capable of rapidly effecting the same change. On adding alcohol to its glycerol solution, betulase is precipitated as a greyish-white powder, the yield being about 0·1 per cent. of the weight of bark taken. The hydrolytic power of betulase is not affected by exposing it for a long period to the air, or by long drying in a desiccator, or even by heating it for several hours at 130°; on the other hand, an aqueous solution of the enzyme rapidly loses its hydrolytic power, especially on being heated. It cannot be dialysed, and becomes turbid when heated or when a mineral acid is added to it. The hydrolytic power of betulase seems to be increased by the presence of small quantities of alkalis or mineral acids, but is diminished by the presence of tannic, picric, or tartaric acid, or of ferric chloride, mercurous nitrate or lead acetate. Mercuric chloride and the sulphates of copper, iron, and zinc are without action. An aqueous solution of betulase does not give a blue coloration with guaiacol, even in presence of hydrogen peroxide; it does not convert starch into sugar, or dissolve albumin or fibrin; neither does it hydrolyse amygdalin, phloridzin, nor salicin. Diastase, emulsin, papayotin, pepsin, or ptyalin do not act on gaultherin. In *Betula lenta*, as in the bitter almond, a glucoside and an enzyme capable of hydrolysing it exist together.

W. A. D.

Action of Rennin. By G. LÖRCHER (*Pflüger's Archiv.*, 1897, **69**, 141—198).—The research gives an account of various methods of obtaining rennin and its zymogen, and of various agencies which modify its activity.

Boiled milk is coagulated more slowly by rennin than fresh milk. The activity of the ferment is diminished by both acids and alkalis,

but an acid reaction raises the resistance to temperature of the ferment.

Rennin is also more resistant to heat in glycerol than in water; the ferment acts between 10° and 60°, but a temperature of 60—70° destroys its activity. The rennin from the frog is active at lower temperatures than that of the calf or human stomach.

The amount of the enzyme is very small during fasting, and still more so in the state of digestion; the amount of the zymogen is, however, considerable. W. D. H.

Classification of Proteids. By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1897, **30**, 3045—3052).—The author gives a scheme for the classification of proteids and allied substances, for which reference must be made to the original.

Halogen Derivatives of Proteids, and their Physiological Relationships. By F. BLUM (*Chem. Centr.*, 1897, i, 181—182; from *Munch. med. Woch.* **43**, 1099).—Stable compounds of proteid are obtainable with iodine, bromine, and chlorine. The iodine compound is stated to be physiologically useful after thyroidectomy, the bromine compound in epilepsy, and the chlorine compound in catarrh and cancer of the stomach. W. D. H.

Halogen Derivatives of Albumin By F. BLUM and WILHELM VAUBEL (*J. pr. Chem.*, 1897, [ii], **56**, 393—396. Compare Loew and Takabayashi, Abstr., 1897, i, 648; Liebrecht, *ibid.*; Hopkins, this vol., i, 54; Hopkins and Brook, *ibid.*, 99).—When a casein solution is warmed with tincture of iodine or with bromine, or treated with chlorine in the cold, and the product is then boiled with aqueous alkali until all the sulphur, and as much halogen as possible, have been removed, the residual product, after precipitation with mineral acids or acetic acid, still contains 2·4—2·6 per cent. of chlorine, 4·8—5·0 per cent. of bromine, or up to 9·7 per cent. of iodine respectively. These numbers correspond to a molecular weight of about 1400 for the product, assuming only one atom of the halogen to be present in the molecule. The amount of ash was very variable; part of the product dissolved in 90 per cent. alcohol and part did not; during the boiling with alkali, ammonia and other gases were evolved, and a smell of thiocarbimides and of trimethylamine was sometimes noticed. When the product of the action of the halogens is heated with 10 per cent. sulphuric acid, instead of with alkali, some halogen is still firmly retained; in neither case is it removed by boiling with silver nitrate. Strong sulphuric acid, and other oxidising agents, do remove it, however. With other proteids—egg-albumin, serum-albumin, protogen, myosin, Witte's peptone, somatose, albumoses, gelatins, &c.—similar results are obtained. C. F. B.

Action of Formaldehyde on Albumin. By A. BACH (*Chem. Centr.*, 1897, i, 420; from *Mon. Sci.*, [iv], 11, i, 157—159. Compare Abstr., 1893, ii, 483).—The author considers that the formaldehyde present in plants is a decomposition product of carbonic anhydride; it seems to be protected from the action of the oxygen liberated simultaneously. To ascertain the cause of this immunity from oxidation, the action of formaldehyde on an aqueous solution of albumin was

studied. A product soluble in water was obtained, the aqueous solution of which was not coagulated by heat, and was less easily precipitable by 95 per cent. alcohol than that of ordinary albumin. If shreds of albumin are dried either in bright sunlight, or at a low temperature, and then dissolved in water, non-coagulable solutions are obtained; in the former case, the solution can be rendered coagulable by the addition of a few drops of acetic acid; in the latter case, by passing a stream of carbonic anhydride. W. A. D.

Separation of Albumoses and Peptone.—By ERNST P. PICK (*Zeit. physiol. Chem.*, 1897, **24**, 246—275).—A detailed account of experiments on the fractional precipitation with ammonium sulphate of solutions of Witte's "peptone." The properties of the various fractions are described, and the general conclusion drawn that Witte's peptone contains several albumoses and peptones. Further details, however, are promised regarding their characters and identification.
W. D. H.

New Colloidal Substances Analogous to Proteids derived from a Nucleo-albumin. By JOHN W. PICKERING (*Compt. rend.*, 1897, **125**, 963—965).—Nucleoalbumin prepared from the thymus of the sheep by Halliburton's method was heated with anhydrous calcium chloride in sealed tubes at 150° for 6 hours. The product is a brown, crystalline powder which has not the properties of proteids, although it still gives a violet coloration with potassium hydroxide and cupric sulphate. It has no lævorotatory power, and does not produce intravascular coagulation. When this product is heated in sealed tubes at 125° for 4 hours with phosphorus pentachloride, it is partially converted into a colloid which, after purification by dialysis, is identical in appearance, chemical reactions, and physiological effects with the synthetic colloids obtained by Grimaux. C. H. B.

Chemistry of Hæmoglobin. By JOHN S. HALDANE (*J. physiol.*, 1898, **22**, 298—306).—When potassium ferricyanide is added to solutions of oxyhæmoglobin or carbonic oxide hæmoglobin, or to blood laked by the addition of water, the gas combined with the hæmoglobin is set free, while methæmoglobin is formed. The oxygen of the blood can be rapidly and accurately determined without the use of the air-pump, by taking advantage of this reaction; a somewhat modified Dupré urea apparatus may be used for this purpose. W. D. H.

Absorption of Violet and Ultra-violet Rays by Hæmoglobin and its Derivatives. By ARTHUR GAMGEE (*Zeit. Biol.*, 1897, **34**, *Jubelband*, 505—528).—A full account, illustrated with photographs of spectra, of researches which have been previously published (Abstr., 1896, i, 713). W. D. H.

Organic Chemistry.

Methyldiethylethylene. By MICHAEL SAYTZEFF, jun. (*J. pr. Chem.*, 1898, [ii], 57, 38—43).—The formation of the heptylene obtained by Baratéeff and Saytzeff (Abstr., 1887, 353) as one of the oxidation products of triethylcarbinol, was probably due to the dehydrating influence of the sulphuric acid used in the oxidising mixture; it seems to be a *methyldiethylethylene*, $CEt_2\colon CHMe$, and can be prepared by heating triethylcarbinol (1 mol.), with oxalic acid (1 mol.), which acts as a dehydrating agent (compare Cahours and Demarçay, Abstr., 1878, 653). The hydrocarbon is a colourless liquid which boils at 97—98°, and has a sp. gr. = 0·72285 at 20°/20°, and = 0·72225 at 20°/0°; on oxidation with potassium permanganate, no trace of a glycol can be obtained, acetic and propionic acids being formed, together with a small quantity of triethylcarbinol. The author concludes that the latter substance is first formed by the addition of $1H_2O$ to the methyldiethylethylene, and that the acetic and propionic acids result from its oxidation. W. A. D.

Aliphatic Nitroso-compounds. By OSCAR PILOTY (*Ber.*, 1898, 31, 452—457. Compare Abstr., this vol., i, 117.)—When acetoxime is dissolved in water and treated with bromine in presence of pyridine, 2-*bromo*-2-*nitrosopropane*, $CBrMe_2\cdot NO$, is formed as a deep blue, mobile liquid, which has an extremely unpleasant, pungent odour; it boils and decomposes at 83°, but can be distilled at 12·5° under a pressure of 26 mm. without alteration. It dissolves readily in benzene, alcohol, &c., but is insoluble in water, and when kept decomposes, forming acetoxime hydrobromide and a liquid which is insoluble in ether, and gives a vapour which has an extremely irritating effect on the mucous membrane. The molecular weight was determined by the freezing point method in benzene solution. The isomeric acetoxime hypobromite, $CMe_2\colon N\cdot OBr$, has not been obtained, but the corresponding hypochlorite is known, and is a colourless liquid. The author concludes from these facts that the blue colour is associated with the presence of the nitroso-group, and that, therefore, the pseudonitroles must also be considered to contain this group.

Several solid nitroso-compounds, such as $C(CH_2\cdot OAc)_3\cdot NO$, and nitroso-octane (see the following abstract), which are colourless in the crystalline state, form colourless solutions in benzene at a low temperature, whilst if the temperature be allowed to rise slightly, the solution becomes blue. A determination of the freezing point of these solutions shows that, in the colourless solution, the nitroso-compound has twice the molecular weight that it has in the blue solution.

A. H.

Nitroso-octane. By OSCAR PILOTY and OTTO RUFF (*Ber.*, 1898, 31, 457—458. Compare the foregoing abstract).—When nitrodi-isobutyl, $NO_2\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CHMe_2$, is reduced with aluminium amalgam in presence of ether, it is converted into 2-*nitroso*-2 : 5-*dimethylhexane*, $NO\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CHMe_2$, which crystallises in compact, colourless,

prismatic plates melting at 54° to a deep blue liquid; it sublimes, without decomposition, above its melting point, and is insoluble in water, acids, and alkalis.

Regularities in the Boiling Points of Isomeric Aliphatic Compounds. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1898, **31**, 313—314).—A reply to Naumann (this vol., i, 221). M. O. F.

Preparation of Absolute Alcohol by means of Calcium Carbide. By PAUL YVON (*Compt. rend.*, 1897, **125**, 1181—1182).—When calcium carbide is added to alcohol which contains water, the carbide is attacked with liberation of acetylene so long as any water remains undecomposed. This reaction can be used for the detection of water in alcohol; acetylene is liberated, and the liquid when shaken becomes turbid, owing to the presence of calcium hydroxide. It can also be employed for the preparation of anhydrous alcohol; for this purpose, alcohol of 90° or 95° is mixed with about one-quarter its weight of the coarsely granulated carbide, well shaken from time to time during 2 or 3 hours, allowed to remain 12 hours, and then decanted and distilled. The first portions of the distillate contain some dissolved acetylene and may be collected separately, or the entire distillate may be shaken with anhydrous cupric sulphate, and redistilled without previously separating the copper acetylide. C. H. B.

Alkylic Sulphites. By ARTHUR ROSENHEIM and OTTO LIEBKNECHT (*Ber.*, 1898, **31**, 405—414).—Contrary to the statement of Warlitz (*Annalen*, 1867, **143**, 72), ethylic sulphite, $SO(OEt)_2$, is decomposed only with extreme slowness by 20 per cent. aqueous potash, and the product is not potassium ethylic sulphite, $OEt\cdot SO\cdot OK$, but potassium ethylsulphonate, $Et\cdot SO_2\cdot OK$, for it yields no sulphurous anhydride when treated with mineral acids. True alkylic sulphites, which the authors formulate as $M'\cdot SO_2\cdot OR$ [$R = Me,Et$; $M' = Na,K$], can be obtained by passing the calculated amount of sulphurous anhydride into alcoholic sodium or potassium methoxide or ethoxide (compare Szarvasy, Abstr., 1897, i, 585). Sodium methylic sulphite will keep for weeks in a well stoppered bottle; the ethylic salt decomposes in about an hour, with evolution of sulphurous anhydride, and potassium ethylic sulphite decomposes as soon as it has become dry, although both of these salts are comparatively stable when in contact with alcohol. Neither propylic, amylic, nor phenylic sulphites can be obtained by this method. The alkylic sulphites exhibit very different reactions from those of the isomeric alkylsulphonates; for example, they are decomposed, even by dilute mineral acids, sulphurous anhydride being evolved. Sodium methylic sulphite is stable in aqueous solution at 0°, but at 25° it is decomposed into methylic alcohol and sodium hydrogen sulphite; the ethylic sulphite undergoes this decomposition even more readily. When heated with ethylic iodide and absolute alcohol at 150°, sodium ethylic sulphite undergoes transformation into the ethylsulphonate; a crystalline product is obtained which has the composition $4EtSO_3Na,NaI$, and can also be prepared by the direct action of sodium iodide on sodium ethylsulphonate.

The ease with which the alkylic sulphites described are hydrolysed

as compared with the difficulty experienced in hydrolysing ethylic sulphite, $SO_2(OEt)_2$, leads to the conclusion that they cannot, like this last substance, have the symmetrical structure $OM'{\cdot}SO{\cdot}OR$, but must rather be formulated as $M'{\cdot}SO_2{\cdot}OR$. C. F. B.

Methyltertiarybutylallylcarbinol. By AL. GNEDIN (*J. pr. Chem.* 1898, [ii], 57, 104—111).—*Methyltertiarybutylallylcarbinol*, obtained by the action of zinc and allylic iodide on pinacolin, is a colourless, mobile liquid smelling strongly of camphor, boils at 168·4° (corr.), solidifies on cooling to four-sided prisms melting at −7°, and has a sp. gr. = 0·85639 at 20°/20°. Although it contains an asymmetric carbon atom, it is optically inactive.

On oxidation with potassium permanganate, it is converted first into a *hydroxy*-derivative, $C_9H_{20}O_3$, crystallising in triclinic plates, and melting at 87—88°, and on further oxidation into an acid having the composition of β-methyltertiarybutylethylenelactic acid.

A. W. C.

Tertiary Nitroisobutylenic Glycol. By GIUSEPPE CESÀRO (*Chem. Centr.*, 1897, ii, 179; from *Bull. Acad. roy. Belg.*, [iii], 33, 323—333).—The author gives the results of a crystallographic examination of the large yellow, and small colourless crystals of tertiary nitroisobutylenic glycol prepared by Henry (Abstr., 1896, i, 4). When heated, this compound loses its crystalline form before melting, melts at 140°, and on cooling suddenly, crystallises at 57°; on again heating and cooling, the same phenomena are exhibited. E. W. W.

Trihydric Alcohol obtained from Dipropylallylcarbinol. By ALEXIS BOGORODSKY (*J. pr. Chem.*, 1898, [ii], 57, 35—38).—1-*Dipropyl*-1 : 3 : 4-*butanetriol*, $OH{\cdot}CPr_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, obtained on oxidising dipropylallylcarbinol (1 mol.) with aqueous potassium permanganate ($1\frac{1}{2}$ mols.), is a viscid, colourless liquid, which is easily soluble in water and alcohol, but only sparingly in ether. On being heated with acetic anhydride, it yields a mixture of its triacetyl compound, and the diacetate of an unsaturated glycol, $CPr_2{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$; these products were, however, not separated. W. A. D.

Formaldehyde or Methylene Derivatives of certain Polyhydric Alcohols and Acids of the Sugar Group. By K. WEBER and BERNHARD TOLLENS (*Annalen*, 1898, 299, 316—340).—A more detailed account of work which has already been published (see this vol., i, 60). M. O. F.

Fermentation of Cellulose. By V. OMELIANSKI (*Compt. rend.*, 1897, 125, 1131—1133).—Pure paper was allowed to ferment in presence of calcium carbonate at a temperature of about 35° for 13 months. The products obtained from 3·4743 grams of paper were :—acids of the acetic series, 2·2402 grams; carbonic anhydride, 0·9722 gram; and hydrogen, 0·0138 gram. The acids were chiefly acetic acid and butyric acid, the ratio of the former to the latter being 1·7 : 1. Small quantities of valeric acid, higher alcohols, and odorous products were formed.

The absence of methane from the products of fermentation is remark-

able, but the formation of this gas seems to be due to a special organism readily distinguishable from the ferment that produces the fatty acids. This organism is at present under investigation. C. H. B.

Ethylnitramine and its Derivatives. By HERM. UMBGROVE and ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1897, **16**, 385—400. Compare Abstr., 1889, 493).—To prepare *diethyldinitro-oxamide*, 5 grams of diethyloxamide are gradually added to 20 c.c. of pure, colourless nitric acid (obtained by distilling nitric acid with sulphuric acid under diminished pressure). The mixture is allowed to remain in a dry atmosphere for several days at the ordinary temperature, and is then poured into a mixture of ice and water. It is extracted with ether, the ethereal solution agitated with dilute sodium carbonate, and then dried with potassium carbonate. The solid residue from the ethereal solution is recrystallised from alcohol; the yield is usually about 93 per cent. of the theoretical. Diethyldinitro-oxamide melts at 35°, is readily soluble in ether, but is only sparingly soluble in light petroleum or cold alcohol. Attempts to nitrate diethyloxamide by the aid of a mixture of nitric and sulphuric acids did not give good results.

The finely powdered nitro-derivative (28 grams) is gradually added to strong aqueous ammonia (90 c.c.), and the temperature is moderated by surrounding the vessel with cold water; after some time, the mixture is filtered, the residue washed, and the colourless filtrate warmed on the water bath; when cold, sulphuric acid (10 per cent.) is added until the solution gives a blue colour with Congo-red paper. The solution is then extracted with ether, and the residue from the ethereal extract, after keeping for some time over sulphuric acid in a vacuum, consists of pure ethylnitramine. Its sp. gr. at $15° = 1·1675$, and when placed in a freezing mixture it solidifies to rhombic plates melting at 6°; it is odourless, and has an acid reaction.

The *potassium, sodium, lithium*, $EtNLiNO_2$, *silver, barium*,

$$[EtN·NO_2]_2Ba + H_2O,$$

zinc $[EtN·NO_2]_2Zn + 2H_2O$, *cobalt*, $+ 2H_2O$, *nickel, cupric*, $+ 2H_2O$, and *mercuric* compounds are described. The zinc, nickel, copper, and mercury derivatives were obtained by double decomposition from the barium compound, since they are decomposed when their aqueous solutions are boiled.

Normal methylethylnitramine, identical with van Dissel's compound (*Rec. Trav. Chim.*, 1894, **13**, 327), is obtained when the potassium derivative (25 grams) is mixed with methylic iodide (30 grams) and methylic alcohol (90 grams), the mixture being first allowed to remain at the ordinary temperature during 2 days, and then boiled on the water bath for 6 hours; it distils at 90·5° under a pressure of 23 mm., and its sp. gr. $= 1·1012$ at 15°; it does not yield a coloration with an acetic acid solution of α-naphthylamine, and does not react with sulphuric acid. When heated in sealed tubes with thirty times its weight of aqueous potash (10 per cent.) for 12 hours at 100°, it is completely decomposed, yielding nitrous acid and ethylamine, which was tested for by Romburg's method. Diethylnitramine may be prepared in a similar manner by the aid of ethylic iodide; it has previously been obtained from unsymmetrical diethylcarbamide (*Rec. Trav. Chim.*,

1887, 6, 149). The authors confirm van Erp's statement that diethylnitramine is practically unacted on when boiled with aqueous potash for some 5 hours. When heated with thirty times its weight of 10 per cent. aqueous potash at 150—160° for 4 hours, complete decomposition ensues, the chief products being ethylamine, nitrous acid, and resinous matter. *Isomethylethylnitramine* is the chief product formed when the silver derivative of ethylnitramine (97 grams) is treated with methylic iodide (69 grams) and absolute ether (500 c.c.); it is also probably formed in small quantity in the preparation of the normal compound. After repeated fractionation under diminished pressure, it is obtained in the form of a colourless liquid boiling at 36—38° under a pressure of 20 mm., and having a sp. gr. = 1·0415 at 15°; it yields a coloration with α-naphthylamine acetate, and reacts vigorously with sulphuric acid. When heated at 100° in sealed tubes with aqueous potash (10 per cent.), the products are nitrogen, methylic alcohol, and a red resin, probably formed by the action of the alkali on acetaldehyde, one of the primary decomposition products. *Isodiethylnitramine* boils at 46—50° under a pressure of 18 mm., has a sp. gr. = 1·000 at 15°, and resembles the isomethyl derivative in all its reactions. J. J. S.

Two Isomerides of Methylethylnitramine. By HERM. UMBGROVE and ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1897, 16, 401—410. Compare preceding abstract.).—The compound formed by the introduction of a methyl group into ethylnitramine by the action of methylic iodide on its silver derivative, is supposed to have the constitution NEt:NO·OMe or $O<\overset{N\cdot Et}{\underset{N\cdot OMe}{|}}$. When heated in a Pfungst tube at 100° for 7 hours with aqueous potash (10 per cent.), it yields nitrogen and methylic alcohol, together with a small quantity of a substance somewhat richer in carbon, probably dimethylacetal, formed by the action of the methylic alcohol on acetaldehyde. A red, resinous substance is also formed, probably by the action of the alkali on acetaldehyde. The second isomeride of methylethylnitramine,

$$NMe{:}NO\cdot OEt, \text{ or } O<\overset{N\cdot Me}{\underset{N\cdot OEt}{|}},$$

is obtained by the action of ethylic iodide dissolved in absolute ether on methylnitramine. After several rectifications under diminished pressure, it boils at 35° under a pressure of 16 mm., and its sp. gr. = 1·044 at 15°. A substance boiling at 78° under a pressure of 18 mm., and melting at about 6°, was obtained as a bye-product. The second isomeride of methylethylnitramine, when heated with aqueous potash in exactly the same manner as the preceding compound, gave nitrogen and ethylic alcohol; methylic alcohol and formic acid were also produced, but in smaller quantities. The methylic alcohol was tested for by a 12 per cent. solution of chromic anhydride, which readily reacts with methylic alcohol, yielding carbonic anhydride, but which gives practically no gas with ethylic alcohol. J. J. S.

Two Inactive 2:4-Diamidopentanes. By CARL D. HARRIES and TAMEMASA HAGA (*Ber.*, 1898, 31, 550—551).—When acetylacetonedioxime is reduced with sodium and boiling alcohol, a 2 : 4-*diamidopen-*

tane, $CH_2\cdot(CHMe\cdot NH_2)_2$, is formed, which, after drying with barium hydroxide, distils at 41—42° under 11—12 mm. pressure; it is a colourless liquid and fumes in the air. Its *hydrochloride*, $C_5H_{14}N_2,2HCl$, *hydrobromide*, *platinochloride*, and *aurochloride* are well-defined, crystalline compounds. The *diacetyl* derivative crystallises in large, thick prisms, melts at 163°, and is practically insoluble in ether. The *dibenzoyl* derivative crystallises in plates and melts at 189°.

When the dioxime is reduced with sodium amalgam and 80 per cent. acetic acid in the cold, the product is a mixture of the above-mentioned diamidopentane and of an isomeride; they are best separated in the form of their diacetyl derivatives. The one already described is a crystalline substance, whereas the isomeric diacetyl derivative is a syrup. When this syrup is hydrolysed with concentrated hydrochloric acid at 150—160,° it is converted into the isomeric 2 : 4-*diamidopentane* and acetic acid. On evaporating the solution, a hygroscopic *hydrochloride* of the base is obtained, which, on benzoylating, yields a *dibenzoyl* derivative. This melts at the same temperature as the dibenzoyl derivative of the first mentioned 2 : 4-diamidopropane, but the two are not identical, since a mixture of them melts at 158°. The isomeric base, after drying over barium hydroxide, boils at 29—30° under a pressure of 9—10 mm. J. J. S.

New Formation of Trioxymethylene. By GIUSEPPE GRASSI-CRISTALDI (*Gazzetta*, 1897, 27, ii, 502—505).—On passing the vapour of monochloracetic acid through a glass tube kept at a low red heat, hydrogen chloride and carbonic oxide are evolved, and a mixture of formic acid, symmetrical dichloromethylic ether, and trioxymethylene is condensed.

It may be supposed that chloracetic acid decomposes on heating in a similar manner to hydroxycarboxylic acids, with elimination of carbonic oxide, hydrogen chloride, and formaldehyde; the latter in part polymerises, giving trioxymethylene, and in part combines with hydrogen chloride, giving the chlorhydrin $CH_2Cl\cdot OH$, which, by loss of water, yields dichloromethylic ether, $(CH_2Cl)_2O$. It may also be supposed that the chloracetic acid first decomposes into carbonic oxide and the chlorhydrin of formaldehyde which, by loss of hydrogen chloride, gives formaldehyde and by loss of water yields dichloromethylic ether. The formic acid produced during the heating is regarded as an oxidation product. W. J. P.

β-Nitrosoketones. By CARL D. HARRIES and LUDWIG JABLONSKY (*Ber.*, 1898, 31, 549—550).—When diacetonehydroxylamine (this vol., i, 123) is oxidised in chloroform solution with yellow mercuric oxide, *β-nitrosoisopropylacetone*, $NO\cdot CMe_2\cdot CH_2Ac$, is formed; it crystallises in long prisms and melts at 75—76°, yielding a deep blue liquid. The oxidation of diacetonehydroxylamine to a nitroso-compound establishes with certainty the constitution of the former, since Piloty and Ruff (this vol., i, 223) have shown that only tertiary aliphatic hydroxylamines can be thus oxidised. Dihydroxylaminotriacetone, when oxidised in a similar manner, yields *dinitrosodi-isopropylacetone* [*dinitrosodiisobutyl ketone*], $CO(CH_2\cdot CMe_2NO)_2$, melting at 132—133°.

J. J. S.

Isolation of Amido-acids. By N. A. ORLOFF (*Chem. Centr.*, 1897, ii, 192—193; from *Pharm. Zeit. Russ.*, 36, 285—289, 301—303).—The author recommends the nickel salts of amido-acids as a convenient means of separating these acids from the decomposition products of proteids such as those contained in plants, and describes the following compounds.

The *nickel salt of alanine*, $(C_3H_7NO_2)_2Ni + 4H_2O$, prepared by boiling an aqueous solution of alanine with nickel carbonate for $1—1\frac{1}{2}$ hours, forms blue crystals, and loses its water of crystallisation at 108—110°; 100 parts of a saturated aqueous solution contain 0·76 parts of the salt. The *nickel salt of glycocine*, $(C_2H_4NO_2)_2Ni + 2H_2O$, is prepared in a similar manner to the preceding compound, and, like it, is easily soluble in hot water; 100 parts of a saturated aqueous solution at the ordinary temperature contain 3·35 parts of the salt. Leucine does not form a nickel salt when boiled with nickel carbonate or hydroxide. Asparagine yields an easily soluble, amorphous, nickel salt. Generally speaking, those amido-acids whose copper salts are easily soluble and difficult to crystallise, form easily crystallisable nickel salts.

The author has isolated tyrosine, glycocine, and leucine from the decomposition products obtained by heating gelatin and albumin respectively with sulphuric acid of 50—80 per cent. strength for $\frac{1}{2}$—2 hours at a temperature below the boiling point. E. W. W.

Action of Cyanacetic Acid on Isovaleraldehyde and Propaldehye. By ERNST STRASSMANN (*Monatsh.*, 1897, 18, 722—736).—When cyanacetic acid (1 mol.) is heated with isovaleraldehyde (1 mol.) in a sealed tube during 1—2 hours at 106°, a *cyanisoheptenoic* acid, $CH_2Pr^{\beta}\cdot CH⁚C(CN)\cdot COOH$ or $CHPr^{\beta}⁚CH\cdot CH(CN)\cdot COOH$, is formed, which crystallises from light petroleum containing ether, in white, deliquescent needles, melts at 53°, and is easily soluble in ether and water. The *silver* salt is very unstable, whilst the *calcium* salt, $(C_8H_{10}O_2N)_2Ca + 2\frac{1}{2}H_2O$, crystallises when its aqueous solution is evaporated in a vacuum, although it is decomposed when the latter is heated. On being heated with aqueous potash, the cyano-acid is resolved into ammonia, malonic acid, and isovaleraldehyde and its condensation products; when distilled alone, carbonic anhydride and *βγ-isohepteno-nitrile*, $CHPr^{\beta}⁚CH\cdot CH_2\cdot CN$, are formed. The latter boils at 80° under a pressure of 18 mm., and at 175° (corr.) under ordinary pressure, and combines readily with bromine, forming a *dibromide*, $C_7H_{11}NBr_2$, which crystallises in iridescent, white plates and melts at 67°. When heated with 10 per cent. aqueous potash, the nitrile is converted into βγ-isoheptenoic acid, $CHPr^{\beta}⁚CH\cdot CH_2\cdot COOH$ (Fittig and Zanner, Abstr., 1890, 589), which was identified by its boiling point, and by its being converted into isoheptolactone when heated with dilute sulphuric acid; together with the isoheptenoic acid a small quantity of the β-hydroxyisoheptoic acid of Fittig and Feurer (Abstr., 1895, i, 206) was formed. Isoheptenoic acid, together with a small quantity of isoheptolactone, are formed when the nitrile is hydrolysed by concentrated hydrochloric acid.

By heating cyanacetic acid (1 mol.) with propaldehyde (1 mol.) in a

sealed tube at 85° during 4—5 hours, a small quantity of methylethylacraldehyde is formed, together with a larger quantity of an unsaturated *cyano-acid*, CHEt:C(CN)·COOH or

CHMe:CH·CH(CN)·COOH,

which crystallises from a mixture of ether and light petroleum in white plates, melts at 64—65°, and is easily soluble in water. When this is heated with 10 per cent. aqueous potash, ammonia is evolved and propaldehyde and malonic acid are formed; when heated alone above 100°, carbonic anhydride is evolved and a *pentenonitrile*, C_5H_7N, obtained, which boils at 147—150°, readily absorbs bromine, and dissolves with difficulty in water and carbon bisulphide, but easily in ether.

W. A. D.

Action of Sulphuric Acid on Elaidic Acid. By ALEX. TSCHERBAKOFF and ALEXANDER M. SAYTZEFF (*J. pr. Chem.*, 1898, [ii], **57**, 27—35).—On adding sulphuric acid (sp. gr. = 1·80) gradually to melted elaidic acid at 50°, and subsequently decomposing with water the product obtained, a hydroxystearic acid is formed, which, from its properties, and those of its sodium, calcium, barium, zinc, and silver salts, appears to be identical with the acid obtained by similarly treating oleic acid (M. and A. Saytzeff, Abstr., 1887, 30). When distilled, it is decomposed, like the latter acid (Abstr., 1888, 815), into a mixture of oleic and isoleic acids. The configuration of the hydroxystearic acid is discussed.

W. A. D.

Preparation of Lactic Acid. By GEORG KASSNER (*Chem. Centr.*, 1897, ii, 20; from *Apoth. Zeit.*, **12**, 325—326)—According to the author, lactic acid cannot well be prepared by adding zinc oxide to a fermenting solution of cane-sugar, partly inverted by the action of tartaric acid, as the oxide stops the fermentation and the original sugar is obtained. The following method is described. 300 grams of cane-sugar and 1·5 grams of tartaric acid are dissolved in 1700 grams of boiling water and the solution kept at 60° for several days. One hundred grams of old cheese mixed with water and a little more than the calculated quantity of calcium carbonate are then added and the fermentation allowed to proceed for about three weeks; after this time only about 21·5 grams of invert-sugar remain unattacked. The mixture is then boiled, and the zinc salt precipitated by adding zinc chloride to the filtrate. From this salt, the acid is obtained by the action of hydrogen sulphide.

E. W. W.

Racemism. By ALBERT LADENBURG [and in part W. HERZ] (*Ber.*, 1898, **31**, 524—528).—The authors describe experiments which lead them to regard *i*-pyrotartaric acid as exhibiting partial racemism. Quinine *l*-pyrotartrate is more readily soluble than the *d*-salt.

It is held by the authors that racemic compounds exist in the liquid state, and that *i*-coniine is a racemic compound, because change of temperature occurs on mixing the *d*- and *l*-bases. Landolt's objection, that the same phenomenon attends admixture of ether and carbon bisulphide, is invalid, owing to the difference in density of these two substances.

M. O. F.

Isomerides of Pyrocinchonic Acid. By ARTHUR H. E. KETTNER (*Chem. Centr.*, 1897, ii, 263—264; from *Diss. Strassburg*, 1897).—In contradiction to the statement of Delisle, the author has proved that pyrocinchonic acid or its anhydride, when warmed with sodium hydroxide, is converted into dimethylfumaric acid (β-methylmesaconic acid) and methylitaconic acid, a state of equilibrium being attained which varies with the concentration of the alkali employed. Dimethylfumaric acid is slightly soluble in cold water and melts at 239—240°. On dry distillation, it is partly converted into pyrocinchonic anhydride, the complete change being effected by the action of acetic chloride under pressure or of bromine in sunlight. The alkaline earth salts are easily soluble in water. The acid does not form an anhydride when boiled with sodium hydroxide, but yields the isomeric acids. Methylitaconic acid is easily soluble in water, melts at 150—151°, and forms slightly soluble alkaline earth salts; when boiled with sodium hydroxide, it is partly changed into the isomeric acids, and with bromine it forms a *dibromide*, $C_6H_8O_4Br_2$, melting at 153° but pyrocinchonic anhydride is not produced. When heated alone, it yields pyrocinchonic anhydride, but by the action of acetic chloride, *methylitaconic anhydride* is obtained; this crystallises from carbon bisulphide, melts at 62—63°, with water forms methylitaconic acid and on heating is converted into pyrocinchonic anhydride.

On reduction, all three isomeric acids yield the same symmetrical dimethylsuccinic acid. E. W. W.

Derivatives of Glutaconic Acid. By GIORGIO ERRERA (*Gazzetta*, 1897, 27, ii, 393—412).—Ethylic cyanacetate reacts with chloroform and sodium ethoxide in a manner analogous to ethylic malonate and in accordance with the equation $2COOEt\cdot CH_2\cdot CN + CHCl_3 + 4NaOEt = 3NaCl + 4EtOH + COOEt\cdot CNa(CN)\cdot CH\colon C(CN)\cdot COOEt$. The reaction proceeds rapidly on the water bath, and after a few minutes heating the product is poured into alcohol, the sodium chloride filtered off, and the filtrate evaporated; the *ethylic sodio-$\alpha\gamma$-dicyanoglutaconate* which separates on cooling is purified by crystallisation from alcohol. It crystallises in thin, colourless needles containing either alcohol or $2H_2O$, melts and decomposes at 265°, and is not decomposed by boiling with water. The corresponding *calcium* compound, $Ca(C_{11}H_{11}N_2O_4)_2 + 4H_2O$, crystallises in long, yellow needles. On treating a hot aqueous solution of the sodio-derivative with hydrochloric acid, *ethylic $\alpha\gamma$-dicyanoglutaconate*, $COOEt\cdot CH(CN)\cdot CH\colon C(CN)\cdot COOEt$, separates and is ultimately obtained in yellow laminæ melting at 178—179.° It is accompanied by a white, crystalline *compound*, $C_{11}H_{16}N_2O_6$, which begins to decompose at 160° and is obtained by boiling the dicyanoglutaconate with alcohol; this probably has the constitution $COOEt\cdot CH(CN)\cdot CH\colon C(CONH_2)\cdot COOEt + H_2O$, and when heated in sulphuric acid solution or with soda yields *diethylic $\alpha\gamma$-cyanocarboxyglutaconate*, $COOEt\cdot CH(COOH)\cdot CH\colon C(CN)\cdot COOEt$ or

$$COOEt\cdot CH(CN)\cdot CH\colon C(COOH)\cdot COOEt,$$

which crystallises in colourless laminæ melting at 191°, and forms a crystalline *sodium* salt, $C_{11}H_{12}NO_6Na + 2H_2O$.

Sodium ethylic αγ-cyanocarboxyglutaconate,

$COOEt\cdot CH(COOH)\cdot CH\colon C(CN)\cdot COONa$ or

$COOEt\cdot CH(CN)\cdot CH\colon C(COOH)\cdot COONa$,

obtained by boiling diethylic cyanocarboxyglutaconate with aqueous soda, crystallises in small, colourless tablets containing $2H_2O$, and when treated with concentrated sulphuric acid and then with water, yields a crystalline precipitate of the corresponding *ethylic dihydrogen* salt. On boiling the liquid, however, carbonic anhydride is evolved and *ethylic αγ-cyanocarboxyvinylacetate*, $COOEt\cdot CH(COOH)\cdot CH\colon CH\cdot CN$ or $COOEt\cdot CH(CN)\cdot CH\colon CH\cdot COOH$, separates; this crystallises in hard prisms melting at 179°, and yields a crystalline *sodium* salt, $C_8H_8NO_4Na$. On adding bromine to a warm aqueous solution of the monethylic salt, *monethylic α-bromo-αγ-cyanocarboxyvinylacetate*,

$COOEt\cdot CBr(COOH)\cdot CH\colon CH\cdot CN$ or

$COOEt\cdot CBr(CN)\cdot CH\colon CH\cdot COOH$

is obtained; it crystallises in white needles.

On boiling monethylic cyanocarboxyvinylacetate with potash and subsequently adding hydrochloric acid, *γ-cyanovinylacetic acid*, $CN\cdot CH\colon CH\cdot CH_2\cdot COOH$, is obtained; it crystallises in yellow prisms melting at 185—195° and is possibly a γ-cyanocrotonic acid of the constitution $CN\cdot CH_2\cdot CH\colon CH\cdot COOH$. W. J. P.

Condensation of Cyanacetamide with Chloroform. By Giorgio Errera (*Gazzetta*, 1897, 27, ii, 412—416).—Cyanacetamide reacts with chloroform and sodium ethoxide, in a manner analogous to ethylic malonate, in accordance with the equation:—

$$2CN\cdot CH_2\cdot CO\cdot NH_2 + CHCl_3 + 4NaOEt =$$
$$NH_2\cdot CO\cdot CNa(CN)\cdot CH\colon C(CN)\cdot CO\cdot NH_2 + 3NaCl + 4EtOH;$$

sodio-αγ-dicyanoglutaconamide, obtained thus, crystallises in yellow needles, and when treated with hydrochloric acid in aqueous solution yields *αγ-dicyanoglutaconamide*, $NH_2\cdot CO\cdot CH(CN)\cdot CH\colon C(CN)\cdot CO\cdot NH_2$, which crystallises in yellow laminæ melting and decomposing at above 280° and containing more than $1H_2O$.

On dissolving the amide in concentrated sulphuric acid, heating to 100°, and precipitating with water, the *amide* of *α-carboxy-γ-cyanoglutaconic acid*, $NH_2\cdot CO\cdot CH(CN)\cdot CH\colon C(CO\cdot NH_2)_2$, separates; it crystallises in yellow laminæ containing $\frac{1}{2}H_2O$. W. J. P.

Formation of Carbonic Oxide from Ethylic Oxalacetate and its Derivatives (IV.) and Ethylic Benzyloxalacetate. By Wilhelm Wislicenus and Max Münzesheimer (*Ber.*, 1898, 31, 551—557).—When ethylic ethoxyoxalacetate, $COOEt\cdot CO\cdot CH(OEt)\cdot COOEt$, is heated in a stream of carbonic anhydride to a temperature of 180°, carbonic oxide is evolved, this evolution becoming much brisker as the temperature reaches 200°; on raising the temperature, *ethylic ethoxymalonate* (b. p. 228°) distils over. When this salt is hydrolysed with the requisite quantity of sodium hydroxide solution, and then neutralised with the requisite quantity of dilute sulphuric acid, *ethoxymalonic acid* is obtained. This is best extracted with ether, and recrystallised from light petroleum (b. p. 35—50°) and ether; it forms colourless, glistening prisms, melts at 123—125°, is readily soluble in water or in ether, and

dissolves but sparingly in light petroleum or benzene. The *barium* and *silver* salts have also been prepared. When ethylic ethoxymalonate is warmed on the water bath with slightly less than the calculated quantity of phenylhydrazine, *phenylhydrazinomalonic acid dihydrazide*, $N_2H_2Ph\cdot CH(CO\cdot N_2H_2Ph)_2$, is formed; this crystallises from glacial acetic acid in yellowish plates melting at 256—257°, and its solution in concentrated sulphuric acid gave a deep red coloration with ferric chloride or potassium dichromate.

When the ethylic salt is heated with aniline (3 mols.) on the water bath, the chief products are *ethoxymalonodianilide* and the *dianilide* of anilidomalonic acid. The latter compound is practically insoluble in hot alcohol, but crystallises from acetic acid in glistening plates, and melts at 246—247.° Conrad and Bischoff have previously (*Annalen*, **209**, 231) described this compound as melting at 162°. The dianilide of ethoxymalonic acid is readily soluble in hot alcohol, from which it may be crystallised; it melts at 170—171°, and gives a reddish-violet colour with sulphuric acid and ferric chloride.

Ethylic ethoxymethylmalonate, $OEt\cdot CMe(COOEt)_2$, is obtained when ethylic ethoxymalonate is treated with sodium, and then with methylic iodide; it distils at 110° under 16 mm. pressure.

Ethylic benzyloxalacetate, $CH_2Ph\cdot CH(COOEt)\cdot CO\cdot COOEt$, obtained by combining ethylic phenylpropionate with ethylic oxalate in the usual manner (*Annalen*, 1888, **246**, 315), is a colourless oil, and cannot be distilled, even under diminished pressure, without undergoing decomposition. Its *copper* derivative, obtained by the action of copper acetate on an alcoholic solution of the ethylic salt, crystallises from hot alcohol in green needles, and melts at 136—138°. When heated to 200°, the ethylic salt loses carbonic oxide, and yields ethylic benzylmalonate, and when hydrolysed with six times its weight of normal sulphuric acid, it yields *benzylpyruvic* acid, melting at 48—50°. The *hydrazone* of this acid crystallises from dilute alcohol in yellowish crystals melting at 149—151°; and when boiled with 10 per cent. alcoholic sulphuric acid yields *benzylindolecarboxylate*, which, after recrystallisation from a mixture of benzene and light petroleum, melts at 144—146°.

Ethylic 1-*phenyl*-4-*benzyl*-5-*pyrazolone*-3-*carboxylate*,

$$NPh<\begin{matrix}CO\cdot CH\cdot CH_2Ph\\ \quad | \\ N{=}C\cdot COOEt\end{matrix},$$

is obtained when ethylic benzyloxalacetate is warmed with the calculated quantity of phenylhydrazine for an hour on the water bath; it crystallises from alcohol in glistening needles, melts at 194°, and gives no coloration with sulphuric acid or ferric chloride. The mother liquor from this compound yields, on the addition of water, the *phenylhydrazone* of ethylic benzyloxalacetate melting at 64—66°.

Ethylic phthalideoxalate (*Annalen*, 1888, **246**, 343), when heated, does not lose carbonic oxide. J. J. S.

Racemic Transformation of Hydrogen Ammonium Malate. By JACOBUS H. VAN'T HOFF and H. M. DAWSON (*Ber.*, 1898, **31**, 528—534. Compare Kenrick, Abstr., 1897, i, 506).—The statement is made by Pasteur that, on evaporating a solution of inactive hydrogen

ammonium malate, a substance first separates having the form and composition of the active salt without exhibiting hemihedral faces; this is followed by the hydrated racemate investigated by Kenrick (*loc. cit.*).

Recognising that the former substance might be a pseudoracemic compound, according to the classification of Kipping and Pope (Trans., 1897, 71, 989), the authors have examined it from this point of view. The result of their experiments shows that the substance in question is a mixture of 3 parts of *l*-malate with 1 part of the *d*-salt.

A mixture of *d*- and *l*-salts is more readily soluble than either of the active compounds alone; the racemate, in the stable form, is less soluble than either of the active salts, but at the temperature of transformation (76°) it is more readily soluble than the mixture.

M. O. F.

Action of Formaldehyde on Uric Acid. By K. WEBER and BERNHARD TOLLENS (*Annalen*, 1898, **299**, 340—346).—Uric acid combines with formaldehyde, yielding (1) a crystalline, sparingly soluble *compound*, $C_7H_8N_4O_5$, containing two molecular proportions of formaldehyde, and (2) an amorphous, very readily soluble *compound*, which contains four or five molecular proportions of formaldehyde. The crystalline derivative forms *barium* and *calcium* salts, which separate initially as white precipitates, and become gelatinous on agitation.

M. O. F.

Condensations of Furfuraldehyde and Furfuracraldehyde. By H. RÖHMER (*Ber.*, 1898, **31**, 281—285).—The condensations were effected by heating the two substances together with acetic anhydride or glacial acetic acid, and then either pouring the product into water and extracting with ether, or adding soda, decomposing the sodium salt with sulphuric acid, and then extracting with ether. With pyruvic acid, furfuraldehyde forms yellow *furfurylidenepyruvic acid*, $C_4OH_3\cdot CH:CH\cdot CO\cdot COOH$, which melts at 110°, and, when heated at 100° with alcohol, yields a yellow *ethylic* salt melting at 44—45°. With sodium phenylacetate, furfuraldehyde forms *furfurylidenephenylacetic acid*, $C_4OH_3\cdot CH:CPh\cdot COOH$; this melts at 143—144°, and, by mixing it with phosphoric chloride and treating the product with piperidine in benzene solution, it can be made to yield a *piperidide*, melting at 105°.

Furfuracraldehyde condenses with acetone in aqueous solution in the presence of a little soda; the yellow product, *furfuracrylideneacetone*, $C_4OH_3\cdot CH:CH\cdot CH:CH\cdot CMeO$, melts at 33—34°, and its yellowish *oxime* at 122—123°; with acetophenone, it condenses to yellow *furfuracrylideneacetophenone*, $C_4OH_3\cdot CH:CH\cdot CH:CH\cdot CPhO$; this melts at 52—53°, and its *semicarbazide* at 59—60°; with sodium acetate, it condenses to the yellowish *furfuracrylideneacetic acid*,

$$C_4OH_3\cdot CH:CH\cdot CH:CH\cdot COOH,$$

melting at 153—154°; with sodium phenylacetate, to yellow *furfuracrylidenephenylacetic acid*, $C_4OH_3\cdot CH:CH\cdot CH:CPh\cdot COOH$, melting at 212—213°; with pyruvic acid, to yellowish *furfuracrylidenepyruvic acid*, which has no well-defined melting point; and with ethylic malonate to *ethylic furfuracrylidenemalonate*, which boils at 210—211° under

33 mm. pressure. The *semicarbazide* of *furfuracraldehyde* is yellow and melts at 215—219°. C. F. B.

Para-ψ-propylnaphthenic Acid (Hexahydrocumic Acid). By WLADIMIR B. MARKOWNIKOFF (*J. pr. Chem.*, 1898, [ii], **57**, 95—103).—*Hexahydrocumic acid*, $C_{10}H_{18}O_2$, prepared by the action of sodium on cumic acid in boiling amylic alcohol solution, forms monoclinic crystals melting at 94·5—95°. It is not readily volatile with steam, is almost insoluble in cold, more soluble in hot water, and readily so in benzene, chloroform, and ether. When heated to its boiling point (269°) for 2 hours, it is converted into an oily isomeride, which is still under investigation.

The *sodium*, *calcium*, *barium*, and *silver* salts are described. The *methylic* salt is a liquid boiling at 234—235°, of sp. gr. = 0·9614 at 0°/0°; the *amide*, which is produced on heating the methylic salt with concentrated ammonia for 20 hours at 100°, forms needle-shaped crystals melting at 169·5—170·5°. The *anilide* crystallises in needles melting at 204—205°. A. W. C.

Derivatives of Cycloheptane. By EDUARD BUCHNER and ANDREAS JACOBI (*Ber.*, 1898, **31**, 399—402. Compare Abstr., 1897, i, 612).—The following salts of hydroxysuberanecarboxylic acid (suberylglycollic acid, 1-hydroxycycloheptane-1-carboxylic acid,

$$\begin{matrix} CH_2\cdot CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2\cdot CH_2 \end{matrix}\!\!>\!C(OH)\cdot COOH,$$

have been prepared :—*sodium*, with $2H_2O$; *calcium* and *barium*, each with $6H_2O$; *lead*, with $\frac{1}{2}H_2O$, and the anhydrous *silver* salt. The acid itself yields paratoluic acid when heated with strong sulphuric acid; when heated at 120—125° with strong hydrochloric acid, it yields chlorosuberanecarboxylic acid, and this, on boiling with alcoholic potash, yields suberenecarboxylic (Δ^1-cycloheptenecarboxylic) acid. This has a striking similarity to the Δ^1-1-ethylcyclopentene-4-carboxylic acid of Einhorn and Willstätter (Abstr., 1894, i, 524); its *amide*, however, melts at 125—126°. It has the character of an unsaturated compound; it decolorises permanganate at once in alkaline solution, and is reduced by sodium in boiling amylic alcohol solution to suburanecarboxylic (cycloheptanecarboxylic) acid, an oil which yields pimelic acid when oxidised, and of which the *amide* melts at 193—194°, almost the melting point of 1-ethylcyclopentane-4-carboxylamide.

C. F. B.

Sulphonals of Cyclic Ketones. By OTTO WALLACH and WALTHER BORSCHE (*Ber.*, 1898, **31**, 338—339).—Cyclic ketones yield sulphonal derivatives which are strictly analogous to those derived from acetone. *Pentanonesulphonal*, $\begin{matrix} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{matrix}\!\!>\!C(SO_2Et)_2$, is prepared by acting on pentanone and ethylic mercaptan with hydrogen chloride, and treating the product with potassium permanganate solution; it separates from hot water in feathery crystals, and from alcohol in thin, nacreous plates melting at 127—128°. *Methylpentanonesulphonal*,

$$C_5H_7Me(SO_2Et)_2,$$

crystallises from dilute methylic alcohol in lustrous, oblique prisms

melting at 110·5—111·5°. *Methylhexanonesulphonal* is sparingly soluble in cold water and melts at 104—105°, whilst *heptanonesulphonal*, prepared from suberone, crystallises from alcohol in compact prisms melting at 136—138°. A. H.

Action of Ammonia on Hexachloroketo-R-pentene (m. p. 28°). By E. C. THEODOR ZINCKE and ALBERT ROHDE (*Annalen*, 1898, **299**, 367—382).—*Amidopentachloroketo*-R-*pentene*, $\begin{matrix}CCl\text{——}CCl_2\\ \| \\ C(NH_2)\cdot CCl_2\end{matrix}\!>\!CO$, or $\begin{matrix}CCl_2\cdot CCl_2\\ | \\ NH_2\cdot C\text{===}CCl\end{matrix}\!>\!CO$, is prepared by dissolving the hexachloroketo-R-pentene which melts at 28° (Abstr., 1897, i, 507) in benzene, and saturating the ice cold solution with dry ammonia; it crystallises from hot benzene in colourless, rhombic leaflets, and melts at 118°. When crystallised from hot water, or from hot dilute hydrochloric or nitric acid, it forms long, colourless needles, and melts at 127°, but recrystallisation from benzene depresses the melting point to 118°. The compound is indifferent towards hydrochloric, nitric, nitrous, and concentrated sulphuric acids, acetic anhydride, and phosphorus pentachloride; it dissolves in alkalis, and the liquid becomes brown when heated, the odour of isonitrile becoming perceptible.

Amidoheptachloroketo-R-*pentane*, $\begin{matrix}CCl_2\cdot CCl_2\\ | \\ NH_2\cdot CCl\text{—}CCl_2\end{matrix}\!>\!CO$, obtained by dissolving the foregoing substance in glacial acetic acid, and saturating the liquid with chlorine, forms lustrous, prismatic crystals, melts at 72°, and boils at 165° under a pressure of 30—33 mm. It is insoluble in cold, aqueous alkali, and is but slowly attacked by the hot liquid; hot concentrated sulphuric acid has no action on the substance.

Dichlorodiketo-R-*pentene* (*dichlorohydroxyketo*-R-*pentinene*),

$$\begin{matrix}CCl{:}CCl\\ | \\ CO\cdot CH_2\end{matrix}\!>\!CO,$$

or $\begin{matrix}CCl{:}CCl\\ | \\ CO\cdot CH\end{matrix}\!\geqslant\!C\cdot OH$, is prepared by the action of stannous chloride on the foregoing ketones; it crystallises from benzene in monoclinic plates and melts at 162°. The substance sublimes in large, lustrous leaflets, and is volatile in an atmosphere of steam; the vapour has an irritating effect on the mucous membrane.

Hexachlorometadiketo-R-*pentane*, $\begin{matrix}CCl_2\cdot CCl_2\\ | \\ CO\text{—}CCl_2\end{matrix}\!>\!CO$, is produced by the action of chlorine on dichloroketo-R-pentene dissolved in glacial acetic acid. It separates from the dilute acid in thick, colourless crystals and melts at 70°; it is readily volatile, and the odour suggests camphor and quinone. Caustic soda converts the substance into trichloracrylic acid, and ammonia gives rise to the *amide* of dichloracetyltetrachloropropionic acid, $CHCl_2\cdot CO\cdot CCl_2\cdot CCl_2\cdot CO\cdot NH_2$, which crystallises from benzene in slender, colourless needles, and melts at 155—156°; reduction with stannous chloride converts this compound into the amide of dichloracetyldichloracrylic acid. M. O. F.

Preparation of Diorthonitrotoluene. By ARNOLD F. HOLLEMAN and J. BOESEKEN (*Rec. Trav. Chim.*, 1897, **16**, 425—428).—A 20 per cent. yield of dinitroparatoluidine $[Me:(NO_2)_2:NH_2 = 1:2:6:4]$ may be obtained from sym.-trinitrotoluene as follows. Fifty grams of trinitrotoluene are triturated with 100 c.c. of alcohol (95 per cent.), and the mixture is slowly added, with constant stirring, to 60—70 c.c. of ammonium hydrosulphide solution (prepared by saturating a 20 per cent. solution of ammonia with hydrogen sulphide). The mixture is immersed in cold water if necessary. The reaction is ended when the liquid only slowly darkens lead acetate paper. The mixture is then evaporated just to dryness on the water bath, and the dinitrotoluidine extracted with boiling hydrochloric acid (sp. gr. = 1·055). After precipitation with ammonia and recrystallisation from 40 per cent. acetic acid, it forms yellowish-red needles melting at 171°. A small quantity (some 2 grams from 200 of trinitrotoluene) of the isomeric *dinitrotoluidine* $[Me:(NO_2)_2:NH_2 = 1:4:6:2]$ may be extracted from the mother liquor after recrystallisation from dilute acetic acid; it melts at 155°. The amido-group can readily be removed from both dinitrotoluidines by the following method. One gram of the nitrated toluidine is dissolved in 10 c.c. of concentrated sulphuric acid, and the solution diluted with its own volume of water, care being taken to keep the mixture cold. The requisite quantity of sodium nitrite, dissolved in the smallest possible quantity of water, is run into the ice cold solution, which is then poured as quickly as possible into 25 c.c. of boiling alcohol (96 per cent.); after the evolution of gas has ceased, the mixture is poured into water and the dinitrotoluene can be collected. Diorthonitrotoluene after recrystallisation from light petroleum melts at 66° (not 60—61°). It has not been found possible to replace any of the hydrogen atoms of the methyl groups in either 2 : 6-dinitro- or 2 : 4 : 6-trinitro-toluene by chlorine. The authors attribute this to the protective influence of the nitro-groups in the ortho-positions. J. J. S.

Phenylethylallylcarbinol. By ALEXIS BOGORODSKY and J. LJUBARSKY (*J. pr. Chem.*, 1898, [ii], **57**, 44—48).—*Phenylethylallylcarbinol*, prepared by leaving phenyl ethyl ketone (1 mol.) and allylic iodide (2 mols.) in contact with zinc turnings during a week, and subsequently decomposing with water, the additive product formed is a mobile, highly refractive liquid, which has a slightly aromatic odour, is insoluble in water, and boils at 238—242°; on oxidation with aqueous potassium permanganate, it yields a trihydric alcohol, $OH\cdot CEtPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$. This is a thick, yellow syrup, which appears to be converted by acetic anhydride into a mixture of its triacetate, and the diacetate of a glycol, $CEtPh:CH\cdot CH(OH)\cdot CH_2\cdot OH$ (compare this vol., i, 291). W. A. D.

Action of Chlorine on Quinones and Quinoneoximes. By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1897, **27**, ii, 572—587).—Whilst quinone yields a tetrachloride or tetrabromide, substituted quinones do not form additive compounds with more than 2 atoms of halogen.

On treating nitroso-orthocresol in chloroform solution with chlorine in the cold, driving off the chloroform by a current of car-

bonic anhydride, allowing the residue to stand, and crystallising from chloroform, a *nitroso-orthocresol dichloride* of the constitution $CO<\begin{matrix}CHCl\cdot CHCl\\CMe{=\!=}CH\end{matrix}>C:N\cdot OH$ is obtained, crystallising in colourless prisms, and melting at 153—154° with decomposition. When heated with aqueous alcohol, it yields a *chloronitrosocresol*, $C_7H_6NO_2Cl$, which crystallises in yellow needles melting and decomposing at 158—159°, and gives Liebermann's nitroso-reaction.

Nitrosometacresol, when similarly treated with chlorine, yields an *a-toluquinoneoxime dichloride*, $CO<\begin{matrix}CHCl\cdot CHCl\\CH{=\!=}CMe\end{matrix}>C:N\cdot OH$, which crystallises in colourless prisms melting and decomposing at 150—152°; on heating with aqueous alcohol, it yields a *chloronitrosocresol*, $C_7H_6NO_2Cl$, which crystallises in colourless needles melting and decomposing at 147—148°, and resembles its ortho-isomeride in general properties.

Nitrosothymol, on treatment with chlorine in chloroform solution, yields a *chloronitrosothymol*, $C_{10}H_{12}NO_2Cl$, which crystallises in yellow needles melting at 162—163° with decomposition, and gives Liebermann's reaction. Nitrosocarvacrol, under similar conditions, yields a *chloro*-derivative, $C_{10}H_{12}NO_2Cl$, which crystallises in yellow needles melting and decomposing at 157—158°. Thymoquinone, on treatment with chlorine, yields a mixture of mono- and dichloro-thymoquinones which could not be satisfactorily separated. Orthodichloroquinone, when treated with chlorine as above, yields only chloranil, whilst the meta- and para-isomerides are not acted on by chlorine. W. J. P.

A New Synthesis of Phloroglucinol. By E. Flesch (*Monatsh.*, 1897, 18, 755—763).—Since phloroglucinol, as usually prepared, is always contaminated with diresorcinol, the author recommends the following method of preparation. Picric acid is first converted into picryl chloride, which is then reduced by tin and hydrochloric acid to symmetrical triamidobenzene; on heating the hydrochloride of the latter (50 grams), in an atmosphere of hydrogen during 8 hours, with water (2—5 litres) from which air has been expelled by boiling, an 80—90 per cent. yield of pure phloroglucinol is obtained (compare Pollak, Abstr., 1894, i, 22).

The symmetrical *triacetamidobenzene* crystallises from alcohol in white rhombic plates, melts at 208° (uncorr.), and is easily soluble in boiling water but insoluble in ether and benzene. W. A. D.

Ethers of Phloroglucinol and a Synthesis of Hydrocotoin. By J. Pollak (*Monatsh.*, 1897, 18, 736—748).—Phloroglucinol dimethylic ether, prepared by Will's method (Abstr., 1888, 457), is easily soluble in most solvents, but separates from its benzene solution on adding light petroleum in colourless crystals which melt at 36—38° (uncorr.); its *benzoyl* derivative, $C_6H_3(OMe)_2\cdot OBz$, is very soluble in the ordinary solvents, but crystallises from light petroleum or dilute alcohol in slender, glistening needles, and melts at 41—43° (uncorr.). On heating the latter compound with benzoic chloride and zinc chloride (compare Ciamician and Silber, Abstr., 1894, i, 409), the benzoyl derivative of hydrocotoin is formed, which melts at 117—118° (uncorr.),

and not at 113° as stated by Hesse (Abstr., 1895, i, 110); it separates from a concentrated alcoholic solution in needles, but when the latter is dilute, in thin, lustrous plates. When boiled with alcoholic potash, it is converted into hydrocotoin; if the latter is heated with acetic anhydride and sodium acetate, there is formed, together with the acetate (compare Hesse, *Annalen*, **199**, 60), a small quantity of *meta-dimethoxy-β-phenylcoumarin*, $C_6H_2(OMe)_2<\begin{matrix}O\text{---}CO\\ CPh\colon CH\end{matrix}$, which crystallises from alcohol in silky needles, melts at 166—167° (uncorr.), and is converted by concentrated hydriodic acid into Kostanecki and Weber's metadihydroxy-β-phenylcoumarin (Abstr., 1894, i, 88).

From this the author concludes that the structure

$COPh{\cdot}C_6H_2(OMe_2){\cdot}OH$ [$COPh : OH : (OMe)_2 = 1 : 2 : 4 : 6$]

must be attributed to hydrocotoin (compare Ciamician and Silber, Abstr., 1894, i, 255).

Phloroglucinol monethylic ether (this vol., i, 16) boils at 220—221° uncorr.) under 30 mm. pressure, does not yield an oxime, and is converted into phloroglucinol diethylic ether by passing hydrogen chloride through its alcoholic solution; when, however, it is heated with ethylic iodide and potash, a viscous oil is obtained, which is probably a mixture of "pseudo-ethers" (compare Herzig and Zeisel, Abstr., 1888, i, 822).

The *diacetyl* derivative of phloroglucinol monethylic ether crystallises from light petroleum in small, colourless plates, and melts at 40—42° (uncorr.); the *dibenzoyl* derivative is moderately soluble in alcohol, ether, and benzene, and crystallises from light petroleum in colourless plates which melt at 75—77° (uncorr.). W. A. D.

Action of Ortho-xylylenic Bromide on Primary, Secondary, and Tertiary Amines. By MAX SCHOLTZ (*Ber.*, 1898, 31, 414—431). —Ortho-xylylenic bromide, $C_6H_4(CH_2Br)_2$, reacts with aniline in chloroform solution at the ordinary temperature, forming *2′-phenyldihydroisoindole*, $C_6H_4{:}(CH_2)_2{:}NPh$, which melts at 165°, and has no basic properties; in the same way, *meta-* and *para-tolyl-* and *paranisyldihydroisoindoles*, melting at 115°, 195°, and 214° respectively were prepared. With benzylamine, the reaction takes place even more readily, and the product, *2′-benzyldihydroisoindole*, melts as low as 41°, and has basic properties, dissolving in dilute hydrochloric acid and forming a *hydrochloride* which melts at 198°. With amines containing CH_3 or other groups in the ortho-position relatively to the NH_2 group, no such ring-formation takes place; orthotoluidine, xylidine [$Me_2 : NH_2 = 1 : 3 : 4$], and pseudocumidine yield respectively *xylyleneditoluidine*, *xylylenedixylidine*, and *xylylenedipseudocumidine*, $C_6H_4(CH_2{\cdot}NHR)_2$, melting at 148°, 106°, and ? (not stated), whilst orthanisidine and α-naphthylamine yield compounds of the type $CH_2Br{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHR$; that formed in the last case melts at 240—242°.

With secondary amines, NHR'_2, or $NH{:}R''$, ortho-xylylenic bromide forms substituted ammonium bromides of the type $C_6H_4{:}(CH_2)_2{:}NR'_2Br$ or $C_6H_4{:}(CH_2)_2{:}NBr{:}R''$, and these react with a molecule of the same or another amine at 200°, and in aqueous or alcoholic solution, yielding diacid bases of the type $C_6H_4(CH_2{\cdot}NR'_2)_2$ or $NR'_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N{:}R''$. *Xylylenediethylammonium bromide* is a syrup, the *aurochloride* melts at

124°, and the *platinochloride* at 225°; *xylylene-di-diethylamine* boils at 170—175° under 20 mm. pressure. *Xylylene-di-isobutylammonium bromide* melts at 273°, the *aurochloride* at 129°, and the *platinochloride* at 208°; *xylylene-di-di-isobutylamine* melts at 56°, and boils above 200° under 20 mm. pressure. *Xylylenepiperidonium bromide* melts at 234° and the *aurochloride* at 130°, the *platinochloride* decomposes above 230°, and the *periodide*, $C_6H_4\colon(CH_2)_2\colon NC_5H_{10}I,I_5$ at 92°; *xylylenedipiperidyl* boils at 190—195° under 20 mm. pressure, the *aurochloride* melts at 204°, the *platinochloride* melts and decomposes at 240°, and the *dimethiodide* melts at 234°; *xylylenepiperidyldiethylamine* boils at 175—180° under 20 mm. pressure, its *dimethiodide* melts at 216°; *xylylenepiperidyldi-isobutylamine* boils at 196—198° under 20 mm. pressure. With secondary amines in which at least one tertiary carbon atom is directly connected with the NH_2 group, a compound of the type $C_6H_4(CH_2\cdot NR'_2)$ is formed at once, even at the ordinary temperature; monomethylaniline yields *xylylene-di-phenylmethylamine*, melting at 110°, and diphenylamine, although less readily, *xylylene-di-diphenylamine*, melting at 179°.

With tertiary amines, ortho-xylylenic bromide forms substituted diammonium bromides, $C_6H_4(CH_2\cdot NR'''Br)_2$. With pyridine, *xylylene-di-pyridonium bromide* is obtained, melting at 134°, the orange *perbromide* of which, $C_6H_4(CH_2\cdot NC_5H_5Br)_2,Br_4$, melts at 141°; the *aurochloride* melts at 240°, the *platinochloride* at 245—246°. Tripropylamine appears to react in a similar manner.

Attention is called to the fact that, in the reaction between ortho-xylylenic bromide and a primary amine, formation of a ring-compound (dihydroisoindole) is prevented by the presence, in one only of the two ortho-positions relatively to the NH_2 group, of methyl (in toluidine, xylidine, and pseudocumidine), OCH_3 (in anisidine), or a second benzene ring (in naphthylamine); presence of phenylic hydrogen in the ortho-position (as in aniline) is, moreover, less favourable to the reaction than that of methylenic hydrogen (as in benzylamine). In the reaction with secondary amines, the formation of a ring-compound (substituted ammonium bromide) is prevented when the NH_2 group is attached even to one tertiary carbon atom, and when it is attached to two of these, even such reaction as does occur takes place yet less readily. C. F. B.

Oxidation of Orthethylamidophenol. By EMIL DIEPOLDER (*Ber.*, 1898, 31, 495—500).—Orthethylamidophenol, $OH\cdot C_6H_4\cdot NHEt$, was prepared by heating orthanisidine, $OMe\cdot C_6H_4\cdot NH_2$, with ethylic bromide for 5 hours at 59°, treating the product with nitrous acid, separating the orthethylanisidinenitrosamine, and converting it into orthethylanisidine, $OMe\cdot C_6H_4\cdot NHEt$ (which boils at 117° under 3 mm. pressure, at 228—229° (uncorr.), under 728 mm.; the hydrochloride melts at 193°); from this, the methyl group was eliminated by heating with fuming hydrochloric acid for 4 hours at 170°.

When orthethylamidophenol is dissolved in twenty times its weight of 12½ per cent. sulphuric acid, and 120—130 c.c. of 10 per cent. sodium dichromate solution (containing $4H_2SO_4$) is gradually added while the mixture is continually shaken, and it is then extracted with

chloroform, the filtered chloroform extract, on concentration, yields *N-ethylphenoxazineorthoquinone*, $C_6H_4<\begin{smallmatrix}O\text{——}C\colon CH\cdot CO\\ NEt\cdot C\colon CH\cdot CO\end{smallmatrix}$, in dark-red crystals, with a green, metallic reflex, and melting at 226°; ethylamine is also formed, and the reaction takes place according to the equation $2C_8H_{11}NO + 3O = C_{14}H_{11}NO_3 + NH_2Et + 2H_2O$. The quinone is reduced, and at the same time acetylated, by zinc dust and acetic anhydride, and *diorthacetoxy*-N-*ethylphenoxazine*, $C_{14}H_{11}NO(OAc)_2$, melting at 110° is formed. Further, it dissolves in sodium hydrogen sulphite solution, and yields a yellow *dioxime* which decomposes at 140° and crystallises with $1\frac{1}{2}H_2O$, and a red *mono-semicarbazone* which melts and decomposes at 243°. When it is warmed with orthophenylenediamine in acetic acid solution, and the acetate which separates is decomposed by boiling with alcohol, orange *N-ethyltriphenazineoxazine*, $C_6H_4<\begin{smallmatrix}-O-\\ NEt\end{smallmatrix}>C_6H_2\lll\begin{smallmatrix}N\\ N\end{smallmatrix}>C_6H_4$, melting at 229°, is obtained. It also reacts with phenylhydrazine, yielding a violet-brown substance, with greenish lustre, which melts at 210—211°. C. F. B.

Diazonium Hydroxide in Aqueous Solution. By ARTHUR HANTZSCH (*Ber.*, 1898, **31**, 340—348).—When pure diazonium chloride is dissolved in water at 0° and treated with a small excess of freshly precipitated silver oxide, a solution of diazonium hydroxide is obtained, free from chlorine and silver, which contains 70—75 per cent. of the calculated amount of the hydroxide, the remainder being present in the residue in the form of silver diazotate. A solution of the hydroxide can also be obtained by treating a solution of diazonium sulphate with the calculated amount of aqueous barium hydroxide, as much as 96 per cent. of the calculated amount of hydroxide being thus obtained in solution when a $\frac{1}{40}$—$\frac{1}{50}$ normal solution of the sulphate is employed. The solutions are colourless when pure, but usually have a faint yellowish tint, and are strongly alkaline, so that they can be readily titrated with acid, methyl-orange being the best indicator. They cannot be preserved for long, since they gradually decompose even in the cold, more rapidly on warming, into phenol and nitrogen, a considerable amount of a resinous diazo-compound being also formed; this yields nitrogen when heated with dilute acids. The solutions are also readily decomposed by animal charcoal, copper powder, alcohol and hydrogen sulphide. Silver nitrate and mercuric chloride produce heavy precipitates, whilst cobalt salts are decolorised. The hydroxide readily forms colouring matters with aqueous and alkaline solutions of α- and β-naphthol, resorcinol, and phloroglucinol, less readily with phenol, or paracresol; catechol and pyrogallol yield colouring matters, but a certain amount of nitrogen is evolved, whilst quinol causes a vigorous evolution of nitrogen but produces no colouring matter. Ammonia gives a deep orange coloration, probably due to the formation of bisdiazoamidobenzene, whilst with aniline, bisdiazobenzeneanilide, $Ph\cdot N_2\cdot NPh\cdot N_2\cdot Ph$, exploding at 80—81° is obtained. Zinc dust converts the hydroxide into phenylhydrazine, the same effect being more slowly produced by sulphurous acid, a diazonium sulphite being probably first formed. The diazonium hydroxides of methyl derivatives

of diazonium chloride are much less stable, whilst it was found impossible to obtain an analogous compound from naphthylamine. The hydroxides derived from halogen substituted bases are, however, more stable but can only be obtained in very dilute solution, because they very readily yield insoluble diazo-oxides or metallic diazotates.

It will be proved in a future communication that diazonium hydroxide is a stronger base than ammonia, and that pure diazobenzene sodium is partially hydrolysed in dilute solution, with formation of the hydroxide, whilst the presence of soda prevents this action; this accounts for the fact observed by Bamberger, who found that the diazotates and isodiazotates, on reduction, behave differently towards phenylhydrazine in dilute solution and in the absence of an excess of alkali. When an excess of alkali is present, under which conditions no hydrolysis occurs, the two compounds behave in a precisely similar manner with phenylhydrazine, both as regards reduction and reaction.

A. H.

The Replacement of one of the Diazo-groups in Diphenyltetrazochloride by Hydrogen. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 479—483).—When an alcoholic solution of diphenyltetrazochloride, prepared by diazotising benzidine in alcoholic solution, is mixed with an alcoholic solution of benzylidenehydrazone in presence of alcoholic potash, one of the diazo-groups is replaced by hydrogen, and the paradiphenyldiazonium chloride, $C_6H_5 \cdot C_6H_4 \cdot N \colon NCl$, thus formed reacts with the hydrazone to form *phenylformazylbenzene*,

$$C_6H_5 \cdot C_6H_4 \cdot N \colon N \cdot CPh \colon N \cdot NHPh,$$

which is a dark violet powder, melts at 174°, and is converted by oxidation with nitrous acid in chloroform solution into tetraphenyltetrazolium chloride. A small quantity of diformazylbenzene is also formed, but this has not yet been obtained quite pure, and will form the subject of a future communication.

A similar reaction occurs when the alcoholic tetrazo-solution prepared from benzidene is treated with an alkaline solution of phenol, the product being *paraphenylhydroxyazobenzene*, $C_6H_5 \cdot C_6H_4 \cdot N \colon N \cdot C_6H_4 \cdot OH$, a brown, microcrystalline powder which melts at about 300°.

A. H.

New Primary Disazo-Dyes of the Benzene Series. By CARL BÜLOW and HANS WOLFS (*Ber.*, 1898, 31, 488—494).—When dimethylamidophenol [$NMe_2 \colon OH = 1 : 3$], in cooled, dilute acetic acid solution is treated with a diazo-solution, $R \cdot N_2 \cdot OH$, a 4-azo-dye,

$$NMe_2 \cdot C_6H_3(OH) \cdot N_2R,$$

is formed; some new compounds of this class are described. When such a compound, in alkaline alcoholic solution at 0°, is treated with another diazo-solution, $R' \cdot N_2 \cdot OH$, the mixture being stirred for some time and then acidified with acetic acid, or saturated with carbonic anhydride, a 4 : 6-disazo-dye, $NMe_2 \cdot C_6H_2(OH)(N_2R) \cdot N_2R'$, is formed; several such compounds are described.

The new compounds described are tabulated below; under 4 and 6 are given the radicles, R and R′ respectively, joined to those positions by the $\cdot N_2 \cdot$ group; the 1 and 3 positions are occupied in all cases by NMe_2 and OH respectively. R and R′ always contain a benzene

nucleus, and the position of substituting groups in this, relative to the $\cdot N_2\cdot$ group, is indicated by the accented numbers. Many of the substances have a greenish surface lustre in addition to the colour mentioned.

4.	6.	Colour.	Melting point.
$2'$-C_6H_4Me		Dark red	125—127°
$4'$-C_6H_4Me		Red	169—170
$2':4'$-$C_6H_3Me_2$		Brownish-red	166—168
Ph	Ph	Brownish-black	136
Ph	$2'$-C_6H_4Me	Reddish-brown	139—140
$2'$-C_6H_4Me	Ph	Brown	124
Ph	$4'$-C_6H_4Me	Dark red	149
$4'$-C_6H_4Me	Ph	Brownish-black	143—144
Ph	$2':4'$-$C_6H_3Me_2$	Brown	142
$2':4'$-$C_6H_3Me_2$	Ph	Dark coloured	161

C. F. B.

Action of Diazomethane on Aromatic Nitro-Bases. By HANS VON PECHMANN and WILHELM SCHMITZ (*Ber.*, 1898, 31, 293—296).—By treating an ethereal solution of diazomethane with nitrosodimethylaniline, *tetramethyldiamidoglyoxime*N-*phenylic ether*,

$$C_2H_2\left(<\begin{matrix}N\cdot C_6H_4\cdot NMe_2\\ | \\ O\end{matrix}\right)_2,$$

is obtained, and can be purified by crystallisation from chloroform; it is red, and melts and decomposes at 245°. Hydrochloric acid of 20 per cent. strength decomposes it into glyoxal, nitrosodimethylaniline, and amidodimethylaniline; nitrosodimethylaniline hydrochloride crystallises out, and the filtrate, when rendered alkaline, deposits *tetramethyldiamidoglyoxaldianil*, $C_2H_2(:N\cdot C_6H_4\cdot NMe_2)_2$, which is yellowish-brown, and melts at 256—257°. Boiling with phenylhydrazine and alcohol, and subsequent addition of acetic acid causes the ether to yield glyoxalosazone. Boiling with alcoholic potash converts it into parazoxydimethylaniline. Zinc and acetic acid reduce it in the cold to paramidodimethylaniline, and warming with chromic anhydride, oxidises it to quinone. *Tetrethyldiamidoglyoxime* N-*phenylic ether* is prepared in the same way as the methyl compound; it is red, and melts at 204°.

With diazomethane, nitrosoaniline yields red *diamidoglyoxime* N-*phenylic ether*, melting at 208°.

Metahydroxyparanitrosodiethylaniline yields dark-green *tetrethyldiamidodimetahydroxyglyoxime* N-*phenylic ether*, which melts at 168°.

C. F. B.

Action of Diazomethane and of Methylic Iodide and Potash on Nitrosophenol. By HANS VON PECHMANN and EUGEN SEEL (*Ber.*, 1898, 31, 296—299).—The action of diazomethane on nitrosophenol gives rise to quinoneoxime methylic ether and paradihydroxyglyoxime N-phenylic ether; the latter is identical with the compound crystallising

in red needles obtained by the action of methylic iodide and potash, by ter Meer, and subsequently by Bridge.

Paradihydroxyglyoxime N-*phenylic ether*,

$$OH\cdot C_6H_4\cdot N{<}\underset{O}{\overset{CH\cdot}{|}}\underset{O\!-\!-}{\overset{CH}{|}}{>}N\cdot C_6H_4\cdot OH,$$

is insoluble in water and in common organic solvents; the solution in phenol is red, and deposits the substance in red needles when treated with alcohol and ether. It is insoluble in dilute acids, but forms a red solution in caustic soda and ammonia. The substance darkens at 210°, and decomposes at 250°. When boiled with alcohol, phenylhydrazine, and a small quantity of dilute acetic acid, the ether yields glyoxalosazone. M. O. F.

Action of Diazomethane on Substituted Nitrosobenzenes. By HANS VON PECHMANN and AUGUST NOLD (*Ber.*, 1898, **31**, 557—565. Compare this vol., i, 75 and 187). The action of substituted nitrosobenzenes on diazomethane has been studied in order to determine whether the nature and position of the substituting groups interfere with the formation of N-glyoxime ethers.

Glyoxime N-paratolylic ether is readily obtained when an ethereal solution of pure paranitrosotoluene is treated with an ethereal solution of diazomethane. *Glyoxime N-orthotolylic ether* crystallises in yellow needles or plates, melts at 188°, and when treated with alcoholic potash yields orthazoxytoluene melting at 59—60°. The authors have prepared a number of substituted hydroxylamines by reducing dilute alcoholic solutions of the nitro-compounds with zinc dust in the presence of ammonium chloride; the best yields (30—35 per cent.) are obtained when only about 5 grams are reduced at a time. On oxidation with chromic mixture, these compounds gave the corresponding nitroso-derivatives. 4-*Nitrosometaxylene*, after distillation in steam, is obtained as a green oil which solidifies when cooled to 0°, and then melts at 47·5°. Glyoxime N-1 : 3 : 4-xylylic ether crystallises in yellow needles melting at 198°. 2-*Hydroxylaminometaxylene* crystallises from light petroleum in colourless needles, melts at 98°, and on oxidation yields 2-*nitrosometaxylene* melting at 144—145°. Hydroxylaminomesitylene melts at 105° when freshly crystallised, but at 95° when kept for 24 hours; Bamberger gives 116°. Nitrosomesitylene crystallises from dilute alcohol in rhombic plates melting at 129° (Bamberger gives 121·5—122·5°); when treated with diazomethane, it is reduced to hydroxylaminomesitylene, and yields no N-glyoxime ether.

1-*Hydroxylamino*-2 : 4 : 6-*tribromobenzene* crystallises in colourless needles, and melts and decomposes at 132°. Formaldehyde, glyoxal, or phenylhydrazine converts it into tribromaniline. When oxidised with chromic anhydride, it yields 1-*nitroso*-2 : 4 : 6-*tribromobenzene* melting at 120°, together with hexabromazoxybenzene and tribromobenzene. The nitroso-compound is sparingly soluble in most solvents, yields green solutions, and is not readily volatile with steam; it gives a red solution when boiled with alcoholic potash, and when treated with phenylhydrazine is reduced to tribromaniline. Glyoxime N-2 : 4 : 6-tribromophenylic ether, after being dissolved in boiling chloro-

form and precipitated with alcohol, forms pale yellow needles melting at 249·5°. It is much more stable than the simple ethers, and is not acted on when boiled with Fehling's solution or with sodium acetate and acetic anhydride. When warmed with alcohol and phenylhydrazine, it yields hydroxylaminotribromobenzene and glyoxalosazone. *Hexabromazoxybenzene* is obtained when the mother liquor from nitrosotribromobenzene is allowed to remain for 2—3 days. After being dissolved in hot benzene and precipitated with alcohol, it forms glistening, reddish-yellow plates melting at 215°. When reduced with zinc dust and alcohol in the presence of ammonium chloride, it yields *hexabromhydrazobenzene*, which crystallises in colourless needles melting at 126—127°. It quickly turns red on exposure to the air, and is readily soluble in most solvents. When warmed with glacial acetic acid (8—10 parts) and finely divided potassium dichromate (1—1·5 parts) for 5—10 minutes on the water bath, it yields *hexabromazobenzene*, which crystallises in red needles melting at 213°.

2-*Nitrosodimethyl*-1 : 3 : 5-*metaxylidine* melts at 104°, and does not react with diazomethane. J. J. S.

Formation of Acetals from Diortho-substituted Aromatic Aldehydes. By EMIL FISCHER and GEORG GIEBE (*Ber.*, 1898, **31**, 545—549).—The authors regard the formation of acetals from aldehydes as analogous to the etherification of acids by the aid of hydrogen chloride and an alcohol. They have, therefore, undertaken experiments in order to determine whether Meyer and Sudborough's generalisations can also be applied to the acetal formation of aromatic aldehydes. The method employed was that previously described (this vol., i, 167). It has been found that, not only orthonitrobenzaldehyde, but also 2 : 5-dichlorobenzaldehyde and 3 : 6-dichloro-2-nitrobenzaldehyde, when treated with a 1 per cent. solution of hydrogen chloride, yield the corresponding acetals more readily than benzaldehyde itself. 2 : 4 : 6-Trimethylbenzaldehyde also yields an acetal, but not quite so readily as benzaldehyde. The amount of acetal formed was determined by separating the acetal from the unaltered aldehyde, by the aid of hydroxylamine.

2 : 5-*Dichlorobenzodimethylacetal* was obtained by dissolving 10 grams of the aldehyde in 40 grams of a 1 per cent. solution of hydrogen chloride in dry methylic alcohol, and allowing the mixture to remain for 22 hours at the ordinary temperature. It boils at 257—258° under a pressure of 750 mm., and when cooled to 0° solidifies, and then melts at 15°; its sp. gr. = 1·274 at 18°. The yield was 83 per cent. of the theoretical.

3 : 6-*Dichloro-2-nitrobenzodimethylacetal* was prepared by dissolving 15 grams of the aldehyde in 75 grams of the warm methyl alcoholic hydrogen chloride solution, and allowing the mixture to remain for 24 hours at the ordinary temperature; the yield was 70 per cent. of the theoretical. It crystallises from light petroleum in needles, melts at 62—63°, and is readily soluble in alcohol or ether. The corresponding *diethylacetal*, $NO_2 \cdot C_6H_2Cl_2 \cdot CH(OEt)_2$, was obtained in a similar manner, but as the aldehyde is only sparingly soluble in ethylic alcohol, a large excess of the latter must be taken (15 grams of alde-

hyde to 400 of alcohol); it crystallises from alcohol in colourless needles melting at 98—99°.

2 : 4 : 6-*Trimethylbenzodimethylacetal* boils at 242—243° (corr.) under 741 mm. pressure, and solidifies in a mixture of solid carbonic anhydride and ether. The yield was 32 per cent. of the theoretical. Under exactly the same conditions, benzaldehyde yields 53 per cent. of benzodimethylacetal boiling at 198—199° under a pressure of 762 mm. (compare Wicke, *Annalen*, **102**, 363). When boiled with 20 times its weight of aqueous hydrochloric acid (2·5 per cent.), it is completely converted into the aldehyde. J. J. S.

2 : 5-Dichlorobenzaldehyde. By ROBERT GNEHM and RUDOLF SCHÜLE (*Annalen*, 1898, **299**, 347—367. Compare Gnehm and Bänziger, Abstr., 1896, i, 432).—2 : 5-*Hexachlorohydrobenzamide*, $(C_6H_3Cl_2\cdot CH)_3N_2$, obtained by the action of alcoholic ammonia on dichlorobenzaldehyde, crystallises from hot acetone in long, silky needles; it melts at 167° (corr.), and is easily resolved into its components.

The *a-naphthylamine* compound of 2 : 5-dichlorobenzaldehyde is odourless, and melts at 111—112° (corr.); the *β-naphthol* compound, $C_6H_3Cl_2\cdot CH(O\cdot C_{10}H_7)_2$, crystallises from glacial acetic acid in white prisms, and melts, evolving gas, at 205°.

Polymeric 2 : 5-*dichlorothiobenzaldehyde* is produced by the action of hydrogen sulphide on 2 : 5-dichlorobenzaldehyde; it is an amorphous powder, which dissolves readily in benzene, chloroform, and glacial acetic acid, and melts at 194—197°.

2 : 5-*Dichloromandelonitrile*, $C_6H_3Cl_2\cdot CH(OH)\cdot CN$, is prepared from potassium cyanide and the sodium hydrogen sulphite compound of dichlorobenzaldehyde; it forms lustrous, white leaflets, and melts at 93°. It is very volatile in an atmosphere of steam.

2 : 5-*Dichloromandelic acid*, $C_6H_3Cl_2\cdot CH(OH)\cdot COOH$, arises from the nitrile under the influence of concentrated hydrochloric acid at 130° in sealed tubes, alcoholic potash being without action on the substance; it crystallises from water in lustrous, white needles, and melts at 84° (corr.).

2 : 5-*Dichlorodiparamidotriphenylmethane*, $C_6H_3Cl_2\cdot CH(C_6H_4\cdot NH_2)_2$, obtained by heating dichlorobenzaldehyde with aniline and concentrated hydrochloric acid on the water bath, crystallises from petroleum, and melts at 107°. The *hydrochloride* crystallises in long needles, and the *sulphate* is sparingly soluble in water and alcohol. The *diacetyl* derivative crystallises from ethylic acetate in white needles, and melts at 212° (uncorr.).

2 : 5-*Dichlorotriphenylmethane*, $CHPh_2\cdot C_6H_3Cl_2$, is produced by condensation of 2 : 5-dichlorobenzaldehyde with benzene; it crystallises from alcohol in long, well-formed prisms, and melts at 87° (corr.). 2 : 5-*Dichlorophenylditolylmethane*, $CH(C_6H_4Me)_2\cdot C_6H_3Cl_2$, separates from alcohol in colourless crystals, and melts at 89° (corr.).

When a cooled solution of dichlorobenzaldehyde and phenol in glacial acetic acid is treated with concentrated sulphuric acid, the liquid becomes yellowish-red, and exhibits fluorescence; water precipitates a resin, which dissolves in soda, and is reprecipitated by carbonic anhy-

dride. Crystallisation from alcohol yields the substance in rosette-like aggregates, but it has not a constant melting point; it probably consists of the condensation product, $C_6H_3Cl_2\cdot CH(C_6H_4\cdot OH)_2$. Similar compounds are obtained from orthocresol and from resorcinol.

2 : 5-*Dichlorotetrethylparadiamidometadihydroxytriphenylmethane*,
$$CH[C_6H_3(NEt_2)\cdot OH]_2\cdot C_6H_3Cl_2,$$
is obtained by heating dichlorobenzaldehyde and diethylmetamidophenol with a solution of zinc chloride in glacial acetic acid during several hours at 130°; it is an amorphous, reddish powder, and exhibits both basic and acidic properties. The *leuco*-compound is prepared by the action of concentrated sulphuric acid, which eliminates $1H_2O$; it is a blue, amorphous substance, and is readily oxidised in air.

2 : 5-*Dichlororosamine* is produced when the leuco-compound is heated with concentrated sulphuric acid at 140—145°, then poured into water, and the filtered liquid boiled with ferric chloride. It separates from the aqueous solution in a gelatinous condition; the *nitrate* forms a bluish-red solution in water, exhibiting yellow fluorescence.

2 : 5-*Dichlorobenzylidenic chloride*, $C_6H_3Cl_2\cdot CHCl_2$, prepared by slowly adding chlorosulphonic acid to a solution of dichlorobenzaldehyde in chloroform, crystallises from chloroform in cubes, and melts at 42°. Fuming sulphuric acid resolves it into dichlorobenzaldehyde and hydrogen chloride.

Although attempts to sulphonate tetramethyldiamido-2 : 5-dichlorotriphenylmethane were unsuccessful, treatment of the leuco-base with the monhydrate of sulphuric acid converts it into a mixture of monosulphonic and disulphonic acids; oxidation of this product with lead peroxide gives rise to an amorphous, greenish-blue colouring matter.

Benzaldehydeorthosulphonic acid, $SO_3H\cdot C_6H_4\cdot COH$, is prepared according D.R.P. 88952 by heating orthochlorobenzaldehyde with sodium sulphite during 6 hours at 170—180°; it is a thick syrup, which does not crystallise in the desiccator. The *sodium* salt crystallises from water in long, well-formed prisms; the *barium* salt crystallises in bundles of long prisms. The *phenylhydrazone* crystallises from water in long, slender needles melting at 174·5° (corr.); the *sodium* salt forms small, yellow needles. The *sodium* salt of the oxime crystallises in prisms containing $1H_2O$.

Benzaldehydeorthosulphonic acid combines with two molecular proportions of numerous amines, forming valuable colouring matters.

M. O. F.

Nitrogenous Derivatives of Benzylideneacetophenone. By JOSEF TAMBOR and F. WILDI (*Ber.*, 1898, **31**, 349—354).—Benzylideneacetophenone readily forms additive compounds with ammonia and primary aromatic amines, but not with aromatic or mixed secondary bases. One molecule of the base reacts either with one or two molecules of benzylideneacetophenone.

Dibenzylideneacetophenonamine, $NH(CHPh\cdot CH_2Bz)_2$, crystallises in small needles melting and evolving gas at 163°, and yields an *acetyl*-derivative, which crystallises in white needles, and melts at 149°. *Dibenzylideneacetophenonenitrotoluidine*, prepared from nitrotoluidine [$Me : NR_2 : NO_2 = 1 : 2 : 5$], crystallises in sulphur yellow needles melt-

ing at 203°. The *compound* with orthonitraniline forms pale red needles melting at 243°, whilst that with metanitraniline melts and decomposes at 238—240° and that derived from paranitraniline at 251—252°. *Dibenzylideneacetophenone-a-naphthylamine* crystallises in well-developed, greenish prisms melting at 180°. No compounds of 1 mol. of benzylideneacetophenone with 1 mol. of any of the foregoing amido-compounds could be obtained, whereas it readily unites with 1 mol. of aniline to form *benzylideneacetophenoneaniline*,

$$CH_2Bz\cdot CHPh\cdot NHPh,$$

which crystallises in white needles melting at 175°. Similar behaviour is shown by paratoluidine, the *compound* with which forms silky needles melting at 172°, and by β-naphthylamine, which forms a *compound* melting at 200°. No other additive compounds could be obtained from the last three amido-compounds. A. H.

Etherification of Phenols and Benzenecarboxylic Acids. By Hans von Pechmann (*Ber.*, 1898, **31**, 501—504).—When an ethereal or alcoholic solution of a benzenecarboxylic acid is poured into an ethereal solution of diazomethane, CH_2N_2, nitrogen is evolved and the acid is completely converted into the methylic salt; this is the case even with mesitylcarboxylic, symmetrical tribromobenzoic, and mellitic acids (with symmetrical trinitrobenzoic acid, the nitro-groups are also attacked), all of which acids contain two substituting groups in the ortho-position relatively to the carboxyl group.

It is suggested that the reaction consists in a union of the diazomethane with the carboxyl group of the acid $R\cdot COOH$, to form a diazo-compound, $R\cdot COO\cdot N_2\cdot CH_3$, which then splits into $R\cdot COOCH_3 + N_2$, direct displacement of the H of the COOH group being thus effected. A similar direct replacement is effected in diortho-substituted acids when these yield metallic salts; from these salts, the ethereal salts can be prepared by treatment with alkylic iodides. Since the ethereal salts of such acids cannot be obtained by the action of alcohol and hydrochloric acid, it must be concluded that the formation of ethereal salts under such circumstances does not consist in a direct replacement, $R\cdot COOH + EtOH = R\cdot COOEt + H_2O$, but is preceded by the formation of an additive compound, $R\cdot C(OH)_2\cdot OEt$ (Wegscheider, Abstr., 1895, i, 499); it is easy to suppose that the formation of such a compound might be hindered by the presence of two groups in the ortho-position, although the direct displacement of the carboxylic hydrogen is not so hindered. C. F. B.

β-Isophenylacetic Acid. By Eduard Buchner and Ferdinand Lingg (*Ber.*, 1898, **31**, 402—403).—When ethylic ψ-phenylacetate, after fractionation under diminished pressure, is heated for 4 hours at 150° in tubes from which the air has been pumped out, and the product is distilled with steam, *ethylic β-isophenylacetate* passes over as an oil which boils at 115° under 15 mm. pressure. This yields anhydrous sodium β-isophenylacetate when it is hydrolysed with sodium ethoxide and a little water; the anhydrous *silver* salt was also prepared. By decomposing the sodium salt with cooled, dilute sulphuric acid, *β-isophenylacetic acid*, $C_8H_8O_2$, is obtained; this melts at 55—56°, is oxidised at once by permanganate in alkaline solution, and, on successive

treatment with phosphorus pentachloride and aqueous ammonia, yields an *amide* which melts at 98° (compare Abstr., 1897, i, 282).

C. F. B.

Calcium Mesitylenate, and the Author's Water of Crystallisation Theory. By THEODOR SALZER (*Ber.*, 1898, 31, 504—505).—Calcium mesitylenate is now found to crystallise with $5H_2O$ when it is precipitated at the ordinary temperature, and so is in accordance with Rule VI. of the author's theory (Abstr., 1895, 488).

A new rule, Rule VIII., is thus enunciated: "The normal calcium salts of all monobasic benzoic acid derivatives with substituting groups in the meta- or para-position, crystallise with at least $3H_2O$, whilst those of acids substituted in the ortho-position crystallise with only $2H_2O$." In analogy with this is the fact that the calcium salts of the substituted salts of the paraconic acids crystallise with $2H_2O$.

C. F. B.

Action of Ethylic Oxalate and Sodium Ethoxide on Substituted Nitrotoluenes. By ARNOLD REISSERT and JOH. SCHERK (*Ber.*, 1898, 31, 387—397. Compare Abstr., 1897, i, 417).—*Paranitrometatolylpyruvic acid*, $NO_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}CO{\cdot}COOH$ [$Me : CH_2 : NO_2 = 1 : 3 : 4$], is formed when a solution of 92 grams of sodium in 1840 grams of absolute alcohol is slowly added to a well-cooled mixture of 292 grams of ethylic oxalate and 302 grams of paranitrometaxylene and the mixture kept at about 40° for 3 days, the acid being best isolated in the manner previously described. The yield is only some 30 per cent. of the theoretical. It separates from glacial acetic acid in small crystals containing 1 molecule of acetic acid, which it loses at 100°, and then melts at 193°. It is sparingly soluble in water, somewhat more readily in benzene or chloroform, and dissolves with the greatest readiness in alcohol, ether, acetone, and acetic acid. The solutions of its alkali salts have a deep-red colour, its *barium* and *calcium* salts are reddish-yellow, its *lead* salt has a bright, orange-yellow colour. Its *phenylhydrazone* crystallises, on the addition of water to its alcoholic solution, in small, hard, yellow crystals melting and decomposing at 150°.

Paranitrometatoluonitrile is the product formed when hydrochloric acid (10 per cent.) is added to a boiling aqueous solution of the acid (1 mol.) and sodium nitrite (2 mols.); it begins to melt at 78°, but is not completely melted below 120°. It dissolves readily in alcohol, ether, acetic acid, or hot water, and, when shaken with concentrated sulphuric acid and benzene containing thiophen, gives a deep-blue solution. When an alkaline solution of orthonitrometatolylpyruvic acid is oxidised with hydrogen peroxide, *paranitrometatolylacetic acid* is formed; this melts at 149°, and is readily soluble in alcohol, ether, acetone, and chloroform. When chromic acid mixture is used as the oxidising agent, *paranitrometatolualdehyde* is formed; this can be purified by distillation with steam, when it crystallises in thin, glistening needles melting at 61°. The yield is very poor. Its *phenylhydrazone* melts at 150°. When paranitrometatolylacetic acid (10 grams) is suspended in water (200 grams) and reduced with 100 grams of hydrochloric acid (10 per cent.) and the requisite quantity of granulated tin, *paramethyl-*

oxindole, $C_6H_3Me{<}{}^{CH_2}_{NH}{>}CO$ [Me : NH = 1 : 4], is the chief product; the mixture is heated for an hour in a reflux apparatus, filtered, the filtrate rendered alkaline and extracted with ether; the residue from the ethereal extract is recrystallised from hot water, and the methyl-oxindole is obtained in the form of needles melting at 168°, its *acetyl* derivative, $C_{11}H_{11}NO_2$, crystallises from water in yellowish needles, and melts at 161°.

Orthonitrometatolylic methylic ether crystallises from light petroleum in glistening needles, melts at 55°, and is readily soluble in the usual organic solvents. Its condensation with ethylic oxalate is best accomplished by the following process. Ethylic oxalate (7·3 grams) is gradually added to a mixture of sodium ethoxide (3·4 grams) which is quite free from alcohol, with dry ether (34 grams), a solution of the methylic ether (8·4 grams) in dry ether is then added, and the whole allowed to remain for 2 days; the mass is extracted with water, and, on acidifying, the aqueous extract, *orthonitrometamethoxyphenylpyruvic acid*, is precipitated; a further quantity may be obtained by extracting the acidified solution with ether. It crystallises from acetic acid in small, yellowish crystals melting at 128°, is sparingly soluble in water, but dissolves readily in ether, alcohol, acetone, or acetic acid.

Ethylic orthonitrophenylacetate, obtained by etherifying the acid formed on oxidising orthonitrophenylpyruvic acid with hydrogen peroxide (Abstr., 1897, i, 417), crystallises from alcohol in long needles melting at 69°.

When ethylic oxalate (29·2 grams) is mixed with a cold solution of sodium (9·2 grams) in absolute alcohol (180 grams), and orthonitrotoluidine (15·3 grams) is added to the mixture, a considerable quantity of *sodium orthonitroparatolyloxamate*,

$$NO_2\cdot C_6H_3Me\cdot NH\cdot CO\cdot COOH\ [Me : NO_2 : NH = 1 : 2 : 4],$$

crystallises out at the end of 24 hours. The *free acid* melts at 179°, and is fairly easily soluble in hot water. Its ethylic salt is obtained when ethylic oxalate is boiled with orthonitrotoluidine.

If, in the above condensation, the substances are used in the proportion of 1 mol. of orthotoluidine, 2 of sodium ethoxide, and 1 of ethylic oxalate, a certain amount of *diorthonitrodiparatolyloxamide* is formed, together with the oxamic acid. It crystallises from acetic acid in small needles, and is very sparingly soluble in the usual solvents.

J. J. S.

Action of Ethylic Oxalate and Sodium Ethoxide on Nitrotolylic Methylic Ether. By ARNOLD REISSERT (*Ber.*, 1898, **31**, 397—398. Compare preceding abstract).—Paranitrometatolylic methylic ether, $NO_2\cdot C_6H_3Me\cdot OMe$ [OMe : Me : NO_2 = 3 : 1 : 4], crystallises from alcohol or light petroleum in yellow needles melting at 51—52°. When this ether (16 grams), in absolute alcoholic solution, is treated with ethylic oxalate (29·2 grams) and a solution of sodium (9·2 grams) in absolute alcohol (184 grams), and the mixture is kept for 3 days in a closed flask at 35—40°, *paranitrometamethoxyphenylpyruvic acid*, $NO_2\cdot C_6H_3(OMe)\cdot CH_2\cdot CO\cdot COOH$, is formed and can be isolated

in the usual manner. It separates from glacial acetic acid in pale yellow crystals containing a molecule of acetic acid and melting at 161°. Its *ethylic* salt melts at 142°, and its *phenylhydrazone* crystallises in yellow needles melting at 107—108°. J. J. S.

α-Acetylcoumarin. By E. Rap (*Gazzetta*, 1897, **27**, ii, 498—502).—On heating a mixture of salicylaldehyde and ethylic acetoacetate with acetic anhydride for 8 hours on the water bath, pouring the product into water, and adding sodium carbonate, *α-acetylcoumarin*, $\begin{array}{l} CH{:}CH\cdot C\cdot CH{:}CAc \\ \vert \qquad\quad \Vert \qquad\quad \vert \\ CH{:}CH\cdot C{-}O{-}CO \end{array}$, is obtained; it crystallises in long, white needles melting at 123—124°, and yields iodoform when treated with iodine and potash. The *phenylhydrazone*, $C_{11}H_8O_2\cdot N_2HPh$, which is readily prepared, crystallises in yellow needles melting at 181—182°.

On treating α-acetylcoumarin with bromine dissolved in carbon bisulphide, addition occurs, followed by evolution of hydrogen bromide and separation of *β-bromo-α-acetylcoumarin*, $C_6H_4<\begin{array}{l} CBr{:}CAc \\ \quad\;\; \vert \\ O{-}{-}CO \end{array}$, which probably results from the decomposition of an intermediate additive product of the constitution $C_6H_4<\begin{array}{l} CHBr\cdot CBrAc \\ \qquad\quad \vert \\ O{-}{-}{-}CO \end{array}$; it crystallises in long needles which melt at 161—162°, decomposes at 166°, and yields salicylic acid on fusion with potash.

On distilling the commercial salicylaldehyde employed, a considerable fraction was obtained at 100—194°; and this, when treated as above with ethylic acetoacetate, yields a substance which crystallises in large prisms melting at 103—104°, apparently identical with the additive compound, $C_7H_6O_2,C_4H_6O_3$, of salicylaldehyde with acetic anhydride obtained by Perkin. It gives a compound with phenylhydrazine melting at the same temperature as the hydrazone of salicylaldehyde. W. J. P.

Action of Aniline on Dihydroxytartaric Acid. By Arnold Reissert (*Ber.*, 1898, **31**, 382—387).—Blank's anilidomalonic acid, $NHPh\cdot CH(COOH)_2$ (D.R.P. 95268), is obtained by the action of aniline on dihydroxytartaric acid. Fifty c.c. of hydrochloric acid (25 per cent.) are carefully added to a mixture of 20 grams of sodium dihydroxytartrate and 1 litre of water, so that no evolution of carbonic anhydride ensues. Aniline (22·5 grams) is added, the mixture left overnight and then extracted 8—10 times with ether. The residue from the ethereal extractions is dissolved in a small quantity of warm alcohol and aniline; on cooling, the *aniline* salt crystallises in the form of small needles melting at 127°; a considerable amount, however, remains in solution and may be precipitated by the addition of light petroleum. The free acid is obtained by dissolving the aniline salt, in the cold, in the least possible quantity of hydrochloric acid (25 per cent.), and then adding an equal volume of water; it is best purified by dissolving it in alcohol and precipitating with light petroleum. When its aqueous solution is boiled for some time, it is decomposed into carbonic anhydride and *anilidoacetic acid* melting

at 125°. The *ammonium* salt is one of the most characteristic salts of anilidomalonic acid.

Anilidomalonanilic acid, NHPh·CH(COOH)·CO·NHPh, is obtained in a somewhat similar manner when a larger quantity, namely, 42 grams, of aniline, is used; at the end of about 2 hours the precipitate is removed, dissolved in very dilute sodium hydroxide solution, and reprecipitated with hydrochloric acid; a further amount may be obtained from the mother liquors. It crystallises in minute needles, melts and decomposes at 157°, is sparingly soluble in the usual organic solvents, and insoluble in water. The reactions of solutions of the ammonium salt with various metallic salts are given. Anilidoacetanilide is obtained when the previous compound is added to 10 times its weight of water, then poured into an equal volume of concentrated sulphuric acid, and the mixture heated in a boiling water bath, when anilidoacetanilide sulphate separates. J. J. S.

Phthalonic Acid. By Carl Graebe and F. Trümpy (*Ber.*, 1898, 31, 369—375).—Phthalonic acid (orthocarboxyphenylglyoxylic acid), $COOH·C_6H_4·CO·COOH$, is best obtained by Tcherniac's method (compare this vol., i, 263, and also 201). Naphthalene (100 grams), potassium permanganate (625 grams), and water (6·25 litres) are boiled for 3—4 hours in a large, leaden reflux apparatus. When colourless, the solution is cooled, the excess of naphthalene removed, and the clear solution, after acidifying with sulphuric acid (222—240 grams H_2SO_4), is evaporated to dryness and then extracted with ether. The ethereal residue consists of phthalic and phthalonic acids, which are easily separated by treatment with a small quantity of water in which phthalonic acid is readily soluble. 80—95 grams of dry phthalonic acid and 8—10 grams of phthalic acid may thus be obtained.

Phthalonic acid crystallises with $2H_2O$, which it loses when heated at 80—100°, more rapidly at 110—120°; in the hydrated form, it begins to melt at 50°, but when anhydrous melts at 144·5° (corr.). It forms syrupy supersaturated solutions with the greatest readiness; a solution saturated at 15° contains 115 parts of the anhydrous acid to 100 parts of water. It is readily soluble in alcohol or ether and sparingly in chloroform. When the acid is heated, the chief products are phthalaldehydic acid and its anhydride, together with phthalic anhydride and diphthalyl, $CO{<}^{\text{—O—}}_{C_6H_4}{>}C{:}C{<}^{\text{—O—}}_{C_6H_4}{>}CO$. On the addition of benzene containing thiophen in solution and of concentrated sulphuric acid to phthalonic acid, an intense red coloration is developed; on adding water, however, the benzene layer becomes colourless. When the acid is evaporated to dryness on the water-bath with an excess of ammonia, a yellow residue is obtained; this dissolves in water, and on the addition of hydrochloric acid, an excess of which is to be avoided, a white precipitate of an *acid*, $C_9H_7NO_4$, is thrown down. This melts and decomposes at 90—100°, is sparingly soluble in water but dissolves in alcohol, yielding an intense yellow solution which becomes deeper in colour on the addition of alkali. Its *calcium* and *silver* salts indicate that it is a dibasic acid, probably having the constitution $COOH·C_6H_4·C(NH)·COOH$.

When an aqueous solution of phthalonic acid is treated with an excess of hydroxylamine hydrochloride (2 mols.) and the requisite quantity of sodium carbonate, and is acidified at the end of two days, crystals of phthalimide are thrown down.

Phthalonic acid oxime, $\begin{matrix} O\text{---}N \\ | \\ CO\cdot C_6H_4 \end{matrix}\!\!>\!C\cdot COOH$, may be obtained by extracting the aqueous solution with ether; it melts at 167—168°, and dissolves in alkalis and alkali carbonates, yielding deep red solutions, which readily decompose on warming, yielding phthalimide and phthalamic acid.

Phthalidecarboxylic acid is formed when phthalonic acid is reduced in alkaline, neutral or acid solution; it is most readily prepared by the aid of zinc and hydrochloric acid. When heated at 200°, it is completely converted into phthalide and carbonic anhydride.

Phthalaldehydic acid is readily obtained by the action of sodium hydrogen sulphite on phthalonic acid. Ten grams of the dry acid, 55 c.c. of a 10 per cent. sodium carbonate solution, and 30 c.c. of a concentrated solution of sodium hydrogen sulphite are warmed together on the water bath, then evaporated to dryness, acidified, and the aldehydic acid extracted with ether. The yield is 55—60 per cent.

J. J. S.

Homophthalic Acid. By CARL GRAEBE and F. TRÜMPY (*Ber.*, 1898, 31, 375—377).—Phthalonic acid (10 grams), red phosphorus (2 grams), hydriodic acid of sp. gr. = 1·67 (12 c.c.), and water (3 c.c.) are heated for 3—4 hours in a reflux apparatus; a further quantity of water (15—18 c.c.) is then added to the hot mixture, which is boiled until all the precipitated acid has dissolved. The solution is filtered hot, and, on cooling, the greater part of the homophthalic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot COOH$, crystallises in a pure state. When heated to about 190°, the acid is converted into its anhydride, and this, when heated at 210—230°, is converted into hydrodiphthalolactonic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot CH\!<\!\begin{matrix} -O- \\ C_6H_4 \end{matrix}\!>\!CO$.

Gabriel's deoxybenzoin-β-carboxylic acid is readily obtained by the action of benzene and aluminium chloride on homophthalic anhydride; 10 grams of the anhydride, 100 of benzene, and 12 of aluminium chloride, are heated for 3 hours in a reflux apparatus, water and hydrochloric acid are added, and the excess of benzene removed by distillation with steam.

J. J. S.

Action of Ethylic Oxalate on Paramidophenol and its Ethers. By ARNALDO PIUTTI and R. PICCOLI (*Ber.*, 1898, 31, 330—336).—According to Castellaneta (Abstr., 1896, 1, 367), oxalic acid and its ethereal salts react with paramidophenols to form a substituted diamide and monamide, but no imide, whereas Wirths (Abstr., 1897, i, 145) states that he obtained a substituted diamide and an imide. The authors have therefore again investigated the action of diethylic oxalate on paramidophenol and its derivatives, and have in no case obtained a derivative of oximide.

Ethylic oxalate and paramidophenol react at 160° to form dipara-

hydroxyphenyloxamide, which has been described by Castellaneta under this name, and by Wirths as oxalylparamidophenol, together with *ethylic parahydroxyphenyloxamate*, $OH \cdot C_6H_4 \cdot NH \cdot CO \cdot COOEt$, melting at 184—185°. The latter crystallises in long, vitreous, monosymmetric prisms [$a : b : c = 0{\cdot}81902 : 1 : 0{\cdot}65750$; $\beta = 84° 23'$]. When heated with hydrochloric acid at 100°, it yields oxalic acid, paramidophenol, and ethylic chloride, whilst concentrated ammonia converts it into *parahydroxyphenyloxamide*, $OH \cdot C_6H_4 \cdot NH \cdot CO \cdot CO \cdot NH_2$, which crystallises in slender, colourless needles, and sublimes and partly decomposes at about 266°. With ethylic oxalate, paranisidine yields *ethylic paramethoxyphenyloxamate*, which melts at 108—109°, and crystallises in lustrous, colourless, asymmetric prisms [$a : b : c = 1{\cdot}61646 : 1 : 1{\cdot}19475$; $\alpha = 95° 44' 54''$; $\beta = 86° 8' 15''$; $\gamma = 96° 18' 43''$.] This compound was described by Wirths as oxalylparanisidine; concentrated ammonia converts it into *paramethoxyphenyloxamide*, $OMe \cdot C_6H_4 \cdot NH \cdot CO \cdot CO \cdot NH_2$, which separates from alcohol in white flakes melting at 241°. Paraphenetidine reacts with ethylic oxalate to form *ethylic parethoxyphenyloxamate* (the oxalylparaphenetidine of Wirths), which melts at 108—110°, and crystallises in large, six-sided, monosymmetric lamellæ [$a : b : c = 1{\cdot}32727 : 1 : 0{\cdot}95580$]. Alcoholic ammonia converts it into *parethoxyphenyloxamide*, which melts at 241·5°, whilst it is decomposed in the normal manner by hydrochloric acid. A. H.

Action of Acetic Anhydride on the Anilides of Dibasic Acids. By HANS VON PECHMANN and WILHELM SCHMITZ (*Ber.*, 1898, **31**, 336—337. Compare this vol., i, 135).—Acetic anhydride in presence of sodium acetate converts oxanilide into vinylideneoxanilide, as already described, but does not act in a similar manner with the anilides of other dibasic acids. Thus carbanilide and malonanilide yield acetanilide, whereas succinanilide is converted into succinanil.

A. H.

Synthesis of Diphenylhydantoin. By W. HENTSCHEL (*Ber.*, 1898, **31**, 508—510. Compare Bischoff and Hausdörfer, Abstr., 1892, 1334).—When carbonylic chloride is passed into a 30 per cent. solution of ethylic phenylamidoacetate in benzene, the carbaminic *chloride*, $COOEt \cdot CH_2 \cdot NPh \cdot COCl$, is formed; it separates from a mixture of petroleum and alcohol in large prismatic crystals, and melts at 60°. The compound is converted into ethylic carbanilphenylamidoacetate by heating with aniline on the water bath, and when this salt is repeatedly crystallised from alcohol, it yields diphenylhydantoin. M. O. F.

Aromatic Sulphonamides. By FRANZ A. H. SCHREINEMAKERS (*Rec. Trav. Chim.*, 1897, **16**, 411—424).—In the preparation of mesitylenesulphonic chloride, the author has always obtained a quantity of a colourless substance insoluble in ether but soluble in chloroform, ethylic acetate, or acetone; this he regards as the sulphonic anhydride. To prepare the amide, a weighed quantity of concentrated ammonia of known strength is placed in a flask and covered with a layer of ether, a portion of the required quantity of the sulphonic chloride is added; after shaking and allowing to remain for some time until the odour

of ammonia has disappeared, a strong solution of the requisite quantity of potassium hydroxide is added to decompose the ammonium chloride; a further quantity of the sulphonic chloride is then added, and the processes repeated until nearly all the ammonia has been converted into the amide. The methylamide and ethylamide may be obtained in a similar manner.

Mesitylenesulphonmethylamide crystallises from dilute alcohol in long needles melting at 89—90°; the yield is some 85 per cent. of the theoretical. *Mesitylenesulphondimethylamide* also crystallises in colourless needles and melts at 45°. *Mesitylenesulphonethylamide* melts at 75°. None of these amides are decomposed by aqueous potash. When heated with water, they all have the property of forming liquids not miscible with water; the temperature of transition for the methylamide is 76—77°, for the dimethylamide, 40—41°, and for the ethylamide, 64—65°; the presence of other substances raises or lowers these transition temperatures.

Pseudocumenesulphonmethylamide is less readily soluble in ether and alcohol than the corresponding mesitylene derivative. It melts at 90—91°, and its transition temperature in water is 79—80°. The *dimethylamide* is even less soluble in ether, and it melts at 115—116°. The *ethylamide* melts at 98°, its transition temperature being 88°. Both monomethyl and monethyl derivatives dissolve in alkalis, but are reprecipitated on the addition of hydrochloric acid.

Metaxylenesulphonic chloride melts at 32° (Jacobsen, *Ber.*, 1877, **10**, 1015, gives 34°), the amide at 137°, and the methylamide at 43°; the latter is readily soluble in alcohol or ether, its transition temperature is 32—33°. The *dimethylamide*, prepared in the usual manner, remains liquid for several weeks, but when placed in a freezing mixture it slowly solidifies, and then melts at 35°.

Parabenzoyloxybenzenesulphonic chloride, obtained by warming Engelhardt and Latschinow's sodium parabenzoyloxybenzenesulphonate (*Zeit. Chem.*, 1868, 76) with phosphorus pentachloride, and recrystallising from ether, melts at 115—116°. The corresponding *amide* is sparingly soluble in ether, alcohol, or water, and melts at 234—236°. If, in the preparation of the amide, an excess of ammonia is employed and the mixture is warmed, benzamide is produced. When the amide is hydrolysed with barium hydroxide solution, *parahydroxybenzenesulphonamide* is formed, and, after recrystallisation from alcohol or water, melts at 176—177°. J. J. S.

Unsaturated Hydrocarbons. By REINHOLD WALTHER (*J. pr. chem.*, 1898, [ii], **57**, 111—112).—On heating benzylic cyanide with benzaldehyde at 200°, the elements of water are given off, and, at a slightly higher temperature, the cyanogen group is hydrolysed and carbonic anhydride eliminated. By a similar reaction, stilbene has been obtained from benzaldehyde and phenylacetic acid, and the author proposes to prepare a number of hydrocarbons and acids by this method. A. W. C.

Paradinitrodibenzyldisulphonic Acid. By CHRISTOPH RIS and CARL SIMON (*Ber.*, 1898, **31**, 354—355. Compare this vol., i, 143).—Sodium dinitrodibenzyldisulphonate is converted by hot concentrated

hydrochloric acid into the hydrogen sodium salt, and not into the free acid, and it appears that it was this salt which was described by Green and Wahl as the free acid (this vol., i, 200); the latter, which can readily be prepared by the action of sulphuric acid on the barium salt, forms a readily soluble, leafy, crystalline mass, which does not deliquesce. The substance described by Green and Wahl as dinitrostilbenedisulphonic acid is also a hydrogen sodium salt, and appears to have the composition $C_{14}H_9N_2O_9S_2Na$, its constitution having not yet been ascertained. The authors claim priority for their work.

A. H.

Fluorescent Substances. By BRONISLAW PAWLEWSKI (*Ber.*, 1898, **31**, 310—311).—The *compound*, $C_{26}H_{18}O_4$, is obtained by heating resorcinol with benzylic chloride on the water bath, and extracting the product repeatedly with water, alcohol, methylic alcohol, and a mixture of alcohol and glacial acetic acid; it is a red, amorphous powder which does not melt below 320°. The alcoholic solution exhibits a beautiful, green fluorescence, and the red solution in alkalis also develops green fluorescence on dilution; it dissolves in warm, concentrated sulphuric acid, forming a yellow solution which exhibits green fluorescence on dilution. The *tetracetyl* derivative is a yellow, amorphous substance which melts at 90—100°. M. O. F.

Paratoluoylorthobenzoic Acid. By HEINRICH LIMPRICHT (*Annalen*, 1898, **299**, 300—315. Compare Abstr., 1895, i, 422).—The *barium* salt of paratoluoylorthobenzoic acid crystallises from water in aggregates of flattened prisms containing $4H_2O$, the crystals becoming opaque in the desiccator without losing water. The *methylic* salt crystallises in rectangular plates and melts at 66°.

Paratoluoylorthobenzoic acetic anhydride, $C_6H_4Me\cdot CO\cdot C_6H_4\cdot COOAc$, obtained by heating dehydrated toluoylbenzoic acid with acetic anhydride on the water bath, forms colourless crystals, and melts at 102°. When heated at 200°, it yields acetic and phthalic anhydrides.

Phenyltolylphthalide, $\begin{matrix}C_6H_4\\|\\CO\cdot O\end{matrix}\!\!>\!CPh\cdot C_6H_4Me$, is produced on warming a solution of toluoylbenzoic acetic anhydride in benzene with aluminium chloride; it separates from ether in transparent crystals and melts at 106°.

Nitroparatoluoylorthobenzoic acid, $NO_2\cdot C_6H_3Me\cdot CO\cdot C_6H_4\cdot COOH$, separates from dilute alcohol in colourless crystals containing $1H_2O$; it melts at 205°, and crystallises from glacial acetic acid in colourless prisms. The *barium* salt contains $1H_2O$, and the *ethylic* salt crystallises from alcohol in prisms and melts at 122°. The *chloride* crystallises in aggregates of colourless needles and melts at 142°; the *amide* decomposes at 200°, and the *anhydride* melts at 203°.

Nitrotoluoylbenzoic acetic anhydride, $NO_2\cdot C_6H_3Me\cdot CO\cdot C_6H_4\cdot COOAc$, separates from alcohol in colourless, prismatic crystals and melts at 145—146°.

Trinitroparatoluoylorthobenzoic acid is obtained by nitrating toluoylbenzoic acid with a mixture of sulphuric and nitric acids.

Amidoparatoluoylorthobenzoic acid, $NH_2\cdot C_6H_3Me\cdot CO\cdot C_6H_4\cdot COOH$,

forms colourless crystals and melts at 163°; the *hydrochloride* and *silver* derivative are crystalline. M. O. F.

Ditolylphthalide. By HEINRICH LIMPRICHT (*Annalen*, 1898, **299**, 286—299).—Ditolylphthalide, $\begin{matrix} C_6H_4 \\ | \\ CO\cdot O \end{matrix}\!\!>C(C_6H_4Me)_2$, is obtained in almost theoretical amount by treating equal parts of toluene and phthalic chloride in carbon bisulphide with aluminium chloride; it separates from alcohol in colourless, transparent crystals and melts at 116·5°.

Phenylditolylmethanecarboxylic acid, $COOH\cdot C_6H_4\cdot CH(C_6H_4Me)_2$, prepared from ditolylphthalide by the action of alcoholic potash and zinc dust, crystallises from dilute alcohol in slender needles, and melts at 168°. The *ethylic* salt softens at 183° and melts at 197—198°.

Tolylmethylanthranol, $C_6H_4<\begin{matrix} C(C_6H_4Me) \\ | \\ C(OH) \end{matrix}>C_6H_3Me$, is produced by the action of concentrated sulphuric acid on phenylditolylmethanecarboxylic acid; it crystallises from alcohol and melts at 117°.

Tolylmethyloxanthranol, $C_6H_4Me\cdot C\begin{matrix} C_6H_3Me \\ O \\ C_6H_4 \end{matrix}C\cdot OH$, obtained by oxidising tolylmethylanthranol with chromic acid in glacial acetic acid solution, forms yellowish, microscopic needles, and melts at 207°. The *acetyl* derivative softens at 50° and melts at 87°.

Tolylmethylanthracene, $C_6H_4<\begin{matrix} C(C_6H_4Me) \\ | \\ CH \end{matrix}>C_6H_3Me$, is formed on heating tolylmethyloxanthranol with zinc dust in an atmosphere of hydrogen; it sublimes in large, transparent, lustrous leaflets, and melts at 191°.

Dinitroditolylphthalide, $\begin{matrix} C_6H_4 \\ | \\ CO\cdot O \end{matrix}\!\!>C(C_6H_3Me\cdot NO_2)_2$, prepared by adding ditolylphthalide to cold fuming nitric acid, crystallises from a mixture of alcohol and ether in lustrous, monoclinic prisms and melts at 132°; the *octonitroditolylphthalide,* which is formed when nitration is effected with a mixture of sulphuric and nitric acids, crystallises in microscopic needles, and melts at 289°.

Diamidoditolylphthalide, $\begin{matrix} C_6H_4 \\ | \\ CO\cdot O \end{matrix}\!\!>C(C_6H_3Me\cdot NH_2)_2$, obtained by reducing the dinitro-derivative with stannous chloride in alcoholic hydrochloric acid, crystallises from alcohol in small, lustrous prisms, and melts at 192°. The *hydrochloride* melts at 280°, and the *sulphate* forms white crystals.

Dihydroxyditolylphthalide, $\begin{matrix} C_6H_4 \\ | \\ CO\cdot O \end{matrix}\!\!>C(C_6H_3Me\cdot OH)_2$, is formed from the diamido-derivative on treating its acid solution with sodium nitrite and warming the liquid with copper powder; it separates from alcohol as a brown, crystalline powder, and decomposes when heated.

Triphenylcarbinoltricarboxylic acid, $OH\cdot C(C_6H_4\cdot COOH)_3$, is prepared by oxidising ditolylphthalide with chromic and acetic acids, removing

the portion of the product which does not dissolve in alkali, and completing the oxidation of the soluble substances with potassium permanganate; it begins to melt, and decomposes, at 165°, becoming solid at 180°, and finally melting at 304°. This decomposition involves the formation of the *lactone*, which yields the *ethylic* salt,

$$CO{<}{}^{C_6H_4}_{O}{>}C(C_6H_4{\cdot}COOEt)_2,$$

melting at 138—139°. The *amide* of the tricarboxylic acid crystallises in long prisms and melts at 309°. M. O. F.

Chloro- and Bromo-derivatives of β-Naphthylamine. By Adolph Claus and Oskar Jäck (*J. pr. Chem.*, 1898, [ii], 57, 1—18).—On passing chlorine into a well-cooled solution of β-acetonaphthalide in chloroform or acetic acid, Claus and Philipson (Abstr., 1891, 461) obtained 1-chloro-2-acetonaphthalide, which was converted by an excess of chlorine into its tetrachloride without forming a dichloracetonaphthalide. When, however, chlorine (2 mols.) was passed into β-naphthylamine dissolved in 80 per cent. sulphuric acid, 1′ : 4′ : 2-dichloramidonaphthalene was obtained. The authors have confirmed the constitution of this compound by converting it, by means of the diazo-reaction, into the 1′ : 4′ : 2-trichloronaphthalene of Armstrong and Wynne (Proc., 1890, 16).

When dry air, saturated with bromine, is passed into a solution of β-naphthylamine in 80 per cent. sulphuric acid, the 1′ : 3′ : 2-dibromonaphthylamine, obtained by Claus and Philipson (*loc. cit.*) by the action of bromine on an acetic acid solution of β-naphthylamine, is formed; in the latter case, however, 1 : 2-bromonaphthylamine was first produced, whereas in the former no trace of a monobromo-derivative can be detected. The authors find also that when 1 : 2-bromamidonaphthalene is dissolved in sulphuric acid, it is not acted on by either chlorine or bromine, and that 1 : 2-chloronaphthylamine is, under the same conditions, also unaffected by chlorine. They hence conclude that, in presence of sulphuric acid, 2 mols. of chlorine or of bromine act simultaneously on β-naphthylamine.

When 1 : 2-chloracetonaphthalide tetrachloride is heated with alcoholic potash or soda, resinous products only are formed; when, however, aqueous sodium hydroxide (1 mol.) is employed, hydrogen chloride is separated, and three isomeric *dichloro-2-acetonaphthalide dichlorides*, $C_{12}H_9Cl_4NO$, are obtained. The first of these (A) melts at 99—100°, and is easily soluble in ether; it is almost the sole product when the temperature of the reaction is not allowed to rise above 65°. At 80°, the second modification (B) predominates; this is insoluble in ether, but crystallises from alcohol in monoclinic pyramids, and melts at 145°. Together with B is formed the third modification (C), which crystallises from alcohol in prisms and melts at 163°. The modification (A) decomposes rapidly in the air with the loss of HCl, forming 1 : 3 : 4-*trichloro-2-acetonaphthalide*, which crystallises from alcohol in colourless, lustrous needles and melts at 220°. The same substance is obtained when the third modification (C) is heated above 100°. The second modification (B) is only decomposed when heated above its melting point, a resinous product being obtained. These facts can be explained

by giving to the modifications A and C either of the formulæ

$$C_6H_4<\begin{matrix}CCl\cdot CCl\cdot NHAc\\ CCl\cdot CHCl\end{matrix} \quad \text{or} \quad C_6H_4<\begin{matrix}CCl_2-C\cdot NHAc\\ CHCl\cdot C\cdot Cl\end{matrix};$$

whilst to the modification B must be attributed the constitution

$$C_6H_4<\begin{matrix}CCl_2\cdot CCl\cdot NHAc\\ CCl{=}CH\end{matrix} \quad \text{or} \quad C_6H_4<\begin{matrix}CCl_2\cdot CCl\cdot NHAc\\ CH{=}CCl\end{matrix}.$$

When 1-chloro-2-acetonaphthalide tetrachloride is heated with an excess of aqueous soda, a *compound*, $C_9H_5ClO_2$, is formed, which appears to be an indene derivative; it sublimes in beautiful, yellow needles, which darken when heated to 120°, and possess no definite melting point. This substance yields a *sodium* salt which crystallises from water in blood-red needles, and a *barium* salt which forms copper-coloured needles. Its investigation is being continued.

1 : 3 : 4-*Trichloro-2-naphthylamine*, obtained by heating the alcoholic solution of its acetyl compound with hydrochloric acid, crystallises in slender, white needles, and melts at 175°.

1-*Bromo 2-acetonaphthalide tetrachloride*, prepared by passing chlorine (2 mols.) into 1-bromo-2-acetonaphthalide dissolved in chloroform, melts and decomposes at 115°.

A *dibromo-β-naphthaquinone* is formed when 1 : 3′ : 4-tribromo-2-naphthylamine is diazotised in hydrochloric acid and the product boiled with water; it crystallises from light petroleum in orange-yellow needles or plates, and on being heated darkens at 120—130° and melts and decomposes at 200°. From the fact that it is not acted on by alkalis or ammonia, whereas 3-bromo-β-naphthaquinone is converted by these reagents into derivatives of α-naphthaquinone (Zincke, Abstr., 1887, 53), its consititution seems to be that of a 4 : 3′-*dibromo*-1 : 2-*naphthaquinone*. This view supports that taken by Claus and Philipson (*loc. cit.*) of the constitution of the tribromonaphthylamine from which it was prepared. 4 : 3′-*Dibromo*-1 : 2-*dihydroxynaphthalene*, formed when the quinone is heated with aqueous sulphurous acid in a sealed tube at 120—130°, crystallises from water in needles, and when heated, decomposes without melting.

1 : 4 : 3′-*Tribromonaphthalene*, prepared by heating dry 1 : 4 : 3′-tribromo-2-diazonaphthalene sulphate with absolute alcohol, crystallises from hot water in iridescent plates, melts at 98°, and sublimes in the form of slender, white needles.
W. A. D.

Some Ethereal Salts and a Crystalline Pseudo-salt of Rhodinol. By Ernst Erdmann (*Ber.*, 1898, 31, 356—360). The ethereal salts of rhodinol are best prepared by the action of the acid chloride on the alcohol in presence of pyridine. The *butyrate* boils at 142—143° under a pressure of 13 mm., the *isobutyrate* at 135—137° under the same pressure, the *isovalerate* at 135—138° at 7 mm., and the *palmitate* at about 260°, under a pressure of 12 mm. When heated with opianic acid, rhodinol yields a *pseudo*-salt,

$$CO<\begin{matrix}C_6H_2(OMe)_2\\ O\end{matrix}>CH\cdot OC_{10}H_7,$$

which crystallises from alcohol in slender needles melting at 48·5°, and is slowly hydrolysed by boiling water.
A. H.

Composition of the Ethereal Oil of Monarda Fistulosa L. By EDWARD KREMERS (*Chem. Centr.*, 1897, ii, 41).—From the red to brownish oil, of sp. gr. = 0·941 at 20°, obtained by distilling *Monarda fistulosa*, the author isolated carvacrol and a red, crystalline substance which melted at 219—223°, and with alkalis behaved like alizarin. Cymene was also detected.

E. W. W.

Composition of the Oil of Monarda Fistulosa L. By E. J. MELZNER and EDWARD KREMERS (*Chem. Centr.*, 1897, ii, 41; from *Pharm. Review*, 1896. Compare preceding abstract).—A table showing the physical properties and content of phenols (carvacrol), of samples of oil prepared at different seasons is given. After the phenols had been removed, the oil, which contains no ethereal salts, was fractionated, and the physical properties of the various fractions are also shown in a table.

E. W. W.

Composition of the Oil of Monarda Punctata L. By W. R. SCHUMANN and EDWARD KREMERS (*Chem. Centr.*, 1897, ii, 42; from *Pharm. Review*, 1896).—By distilling *Monarda punctata L.* with steam, the author has obtained a pale yellow oil which has an odour of mint, sp. gr. = 0·9307 at 20° and specific rotatory power $[\alpha]_D = +0·0588°$. The oil yielded 56 per cent. of thymol when shaken with sodium hydroxide solution and the remaining oil had a sp. gr. = 0·887 at 20° and specific rotatory power $[\alpha]_D = +1·716°$; cymene was detected in the first fractions of this oil, and linalool or a similar compound in the higher fractions.

E. W. W.

Composition of the Oils obtained from Sassafras Bark and from Sassafras Leaves. By FREDERICK B. POWER and CLEMENS KLEBER (*Chem. Centr.*, 1897, ii, 42; from *Pharm. Review*, 1896).—By distilling the air-dried sassafras bark, 7·4 per cent. of a yellow to a reddish-yellow oil of sp. gr. = 1·075 at 15° and rotatory power $[\alpha]_D = +3° 16'$ (100 mm. tube) was obtained, whilst the roots, freed from bark, yielded only 0·9 per cent. of oil. About 78 per cent. of safrole was obtained from the oil by freezing. By shaking the residual oil with sodium hydroxide solution, 0·5 per cent. of eugenol was isolated, and, finally, 10 per cent. of pinene and phellandrene together was found in the lower fractions, but neither dipentene nor cineol could be detected. The so-called safrene is apparently a mixture of pinene with a little phellandrene. The higher fractions of the oil obtained from the root contain dextrorotatory camphor, and the last fractions give a violet coloration with sulphuric acid and glacial acetic acid, but as the sesquiterpene contained in the oil from the bark does not yield a solid hydrochloride, the presence of cadinene is doubtful. The content of camphor (6·8 per cent.) was estimated by reducing to borneol, converting into the ethoxy-derivative and saponifying.

Only 0·028 per cent. of a pale yellow oil was obtained from the leaves; it had the odour of lemons, a sp. gr. = 0·872 at 15° and rotatory power $[\alpha]_D = +6° 25'$. When the oil was shaken with sodium hydrogen sulphite, a crystalline substance was formed which yielded citral on being decomposed. By heating the residual oil with alcoholic

potassium hydroxide solution and distilling in steam, a paraffin melting at 58° remained behind, and in the alkaline solution acetic and isovaleric acids were detected. The lower fractions of the oil contain, besides pinene and phellandrene, the aliphatic terpene myrcene (compare *Pharm. Rund.*, March, 1895); the higher fractions of the saponified oil contain linalool and geraniol, and the last distillates a sesquiterpene which does not yield a solid hydrochloride. E. W. W.

Guaiacum Resin. I. By JOSEF HERZIG and F. SCHIFF (*Monatsh.*, 1897, **18**, 714—721).—The results summarised in a previous paper (Abstr., 1897, i, 254) are dealt with at length.

The acid of guaiacum resin (guaiaretic acid) is best prepared by extracting the resin (1 kilogram) successively with sodium hydrogen carbonate (500 grams), water, and ether, then dissolving it in benzene (1 kilogram), and adding light petroleum (5 litres); a resinous mass is precipitated, which is filtered off and the solution evaporated, the residue being dissolved in alcohol and alcoholic potash added; after 24 hours, 60 grams of potassium guaiarate has separated, more (16 grams) of this being obtained from the mother liquor, and (50 grams) from the precipitate formed as above on the addition of petroleum to the benzene solution. A much cleaner product is obtained by this method than by that of Hlasiwetz (compare Doebner and Lücker, Abstr., 1897, i, 65).

The authors show that the benzoyl derivative described as a monobenzoate by Doebner and Lücker (*loc. cit.*) is really a *dibenzoate*, $C_{20}H_{24}O_4Bz_2$, analogous to the diacetate described in the previous paper; it melts at 132—135°, not at 131°. They are unable to confirm the statement that guaial (tiglic aldehyde) is formed on distilling guaiaretic acid, guaiacol and pyroguaiacin alone being obtained. Methylic chloride and catechol are formed when guaiaretic acid is heated with hydrochloric acid and acetic acid at 140°; a small quantity of *norguaiaretic acid*, $C_{18}H_{22}O_4$, was also formed. The latter is best prepared by heating guaiaretic acid with concentrated hydriodic acid (b. p. = 127°), and separates from dilute alcohol in white needles, melts at 185°, and yields a *tetracetate*, $C_{18}H_{18}(OAc)_4$, which crystallises from alcohol in white needles and melts at 100—102°.

Analyses of the compounds described point to the formula $C_{20}H_{26}O_4$ for guaiaretic acid, rather than $C_{20}H_{24}O_4$, as given by Doebner.

W. A. D.

Morin, and the Constitution of Flavone Derivatives. By JOSEF HERZIG (*Monatsh.*, 1897, **18**, 700—713).—Since morin differs from quercetin and other flavonol derivatives in colour, and in its behaviour with bromine in acetic acid or alcoholic solution, and with acetic anhydride, the author considers that it cannot have the formula $\begin{array}{l}\mathrm{CH(OH)\cdot CH\cdot C{-}O\cdot C\cdot C_6H_3(OH)_2} \\ \mathrm{CH\cdot CH(OH)\cdot C\cdot CO\cdot C(OH)}\end{array}$ [C:OH:OH = 1:2:4], attributed to it by Perkin (Trans., 1896, 792). He also discusses the influence of the hydroxyl groups in determining the properties of flavonol derivatives, and considers that, amongst this class of compounds, should be included, at present, only substances which closely resemble chrysin and fisetin in physical as well as chemical properties.

It is pointed out that Perkin (*loc. cit.*), in his determination of the

methoxyl groups in tetrabromomorin ethylic ether, omitted to allow for the 2 mols. of water which the ether retains after being dried either in a vacuum or at 100°. That this water is retained by the crystals only, and not chemically as a hydrate, is shown by an analysis of the *tetracetyl* derivative of the ether, $C_{15}H_5Br_4O_2(OAc)_4 \cdot OEt$, which is anhydrous, and melts at 116—120°.

Tetrabromomorin, prepared by the action of bromine on morin in acetic acid solution, melts at 258°, and is identical with the product obtained by Benedikt and Hazura (Abstr., 1885, 533) by the hydrolysis of its ether. Tetrabromomorin ethylic ether, on digestion with hydriodic acid, is reduced to morin, which melts at 285°; under similar conditions, dibromoquercetin tetrethylic ether and dibromorcinol diethylic ether are converted into quercetin and orcinol respectively.

The author points out that, although tetrabromomorin is rapidly converted into its monethylic ether when bromine is added to its alcoholic solution, no such change takes place on heating it with alcohol and hydrochloric or hydrobromic acid, morin, under the same conditions, being also unaffected. The formation of tetrabromomorin monethylic ether by the action of bromine on morin dissolved in alcohol is therefore due to a specific action of bromine.

W. A. D.

Occurrence of Choline and Trigonelline in Strophanthus Seeds. Preparation of Strophanthin. By HERMANN THOMS (*Ber.*, 1898, 31, 271—277).—The seeds of *Strophanthus hispidus* (which are used in West Africa for preparing arrow-poison) were powdered in a mortar, freed from fat and oil, of which they contain 25 per cent., by pressing and washing with light petroleum, and extracted with cold 70 per cent. alcohol in a percolator. The alcohol was distilled off, the residue extracted with water, and lead acetate added to the aqueous extract so long as a precipitate was produced. To the filtered solution, pure ammonium sulphate was added cautiously, in order to precipitate the excess of lead, and then a large excess of powdered ammonium sulphate; the strophanthin separates in flakes, which collect on the walls as a pasty mass; it is purified by repeated solution in alcohol and precipitation with ether. So prepared, it is amorphous, free from nitrogen, and neutral in reaction; it is very poisonous.

The filtrate from the strophanthin was acidified strongly with sulphuric acid, mixed with potassium bismuthiodide solution, and the precipitate, after being washed with dilute sulphuric acid, was decomposed with silver carbonate and water, and the filtered solution mixed with hydrochloric acid, again filtered, and evaporated to crystallisation. In this way, the hydrochlorides of the two bases were obtained; one of them, which is soluble in absolute alcohol, is choline hydrochloride; the other, of which 4·2 grams were obtained from 3 kilos. of seeds, is insoluble in alcohol, and was found to be identical with the hydrochloride of trigonelline (Jahns, Abstr., 1888, 166), the methylbetaine of nicotinic acid.

C. F. B.

Choline and Trigonelline in the Seeds of Strophanthus Kombé. By HERMANN THOMS (*Ber.*, 1898, 31, 404).—The presence of these bases has been shown in the same manner as in the case of *S. hispidus* (preceding abstract).

C. F. B.

Strophanthin. By Leopold Kohn and Victor Kulisch (*Ber.*, 1898, 31, 514—516).—The authors ascribe to strophanthin the empirical formula $C_{31}H_{48}O_{12}$. Hydrolysis with mineral acids resolves it into strophanthidin, along with a product which reduces Fehling's solution, but gives none of the characteristic reactions of dextrose.

M. O. F.

Strophanthin and Strophanthidin. By Franz Feist (*Ber.*, 1898, 31, 534—541. Compare preceding abstracts).—Strophanthin from kombé seeds has the properties previously described by Fraser (Abstr., 1887, 1115; 1888, 606; 1890, 262). It is free from nitrogen, does not reduce Fehling's solution, is optically inactive, readily absorbs moisture, and is capable of forming several hydrates. It loses part of this water when placed over sulphuric acid or when gently warmed, but the last portions of water are difficult to remove. After drying over sulphuric acid, it melts and decomposes at 170°; the author suggests the formula $C_{32}H_{48}O_{16}$. When hydrolysed, strophanthin yields strophanthidin which is insoluble in water, and a compound, $C_{13}H_{24}O_{10}$, which is readily soluble in water, besides a sugar or mixture of sugars; it has been proved that only minute quantities of glucose exist in the hydrolysed solution. The compound, $C_{13}H_{24}O_{10}$, melts at 207°, dissolves with the greatest readiness in water, is also soluble in hot ethylic alcohol or acetone, very sparingly in methylic alcohol, and practically insoluble in ether or light petroleum; it reduces Fehling's solution only after prolonged boiling, does not react with phenylhydrazine, is not directly fermented by yeast, and is slightly dextrorotatory $[\alpha]_D = +8° 24'$ (in 5·76 per cent. solution). On oxidation, it yields oxalic acid, but neither saccharic nor mucic acid, and when boiled with hydrochloric or with sulphuric acid at 120°, it gives a product which reduces Fehling's solution. When benzoylated by the Schotten-Baumann method, it yields a *dibenzoyl* derivative melting at 136°, and a *compound*, $C_{20}H_{22}O_8$, melting at 68°.

A solid sugar melting at 95° was also isolated from the aqueous solution; it was separated from the compound, $C_{13}H_{24}O_{10}$, by its solubility in methylic alcohol. It reduces Fehling's solution, but does not yield a sparingly soluble osazone.

Strophanthidin melts at 169—170°, decomposes at 176°, and on again cooling melts at 232°. It has the composition $C_{26}H_{38}O_7 + 1\frac{1}{2}H_2O$, and on drying readily loses $1H_2O$. It dissolves in concentrated sulphuric acid, yielding a brick-red solution, does not reduce Fehling's solution, and decolorises bromine but slowly. When oxidised with chromic anhydride, it yields benzoic acid, but on oxidation with alkaline permanganate the chief products are oxalic and acetic acids. When hydrolysed by boiling with alkali solution and then acidified, a mixture of two compounds is obtained. The chief product ($C_{24}H_{30}O_5 + 1\frac{1}{2}H_2O$) is a yellow, crystalline substance melting and decomposing at 294°; in the anhydrous form, it decomposes at 350—360° without melting. When freshly prepared, it is readily soluble in sodium carbonate, but after some time it can only be dissolved by warming with alkali; it is readily soluble in alcohol and acetone, more sparingly in methylic alcohol, and is insoluble in light

petroleum or ether. When heated with a 3 per cent. solution of hydrogen chloride in alcohol, it yields a white, amorphous substance with a high melting point.

A second compound, $(C_7H_{10}O_2)x$, obtained on hydrolysis, is much more readily soluble in methylic alcohol; it crystallises in needles, melts at 198·5°, and is insoluble in sodium carbonate, but dissolves in sodium hydroxide solution. It dissolves in concentrated sulphuric acid, yielding a brick-red solution, and on the addition of water a blue, flocculent precipitate is obtained. It is also soluble in concentrated nitric acid, and the addition of water to this solution causes no precipitate (difference from strophanthidin).

Bromine reacts with an ethereal solution of strophanthidin, yielding two bromo-compounds, one, $C_{39}H_{51}Br_5O_{10}$, colourless and melting at 126°, the other, $C_{39}H_{33}Br_{11}O_4$, yellow, and melting at 160°. Both are readily soluble in chloroform, acetone, alcohol, or ether, but insoluble in water or light petroleum. When oxidised with bromine and sodium hydroxide, strophanthidin yields a *dibasic acid*, $C_{39}H_{54}Br_2O_{10}$, melting at 163°.

Alkaline permanganate converts strophanthidin into an amorphous substance, soluble in alkali, alcohol, and chloroform, but insoluble in water, ether, light petroleum, or cold acetone. Its melting point is above 300°. J. J. S.

Gambierfluorescein and Gambier-catechu-red. By KARL DIETERICH (*Chem. Centr.*, 1897, ii, 50—51; from *Ber. Pharm. Ges.*, 7, 153—161).—*Gambierfluorescein* is prepared by moistening 5 grams of gambier-catechu with water, decomposing with 20 per cent. sodium hydroxide solution, and shaking with benzene or ether; the latter dissolves, not only the fluorescein, but also two other substances, the one of an oily and the other of a waxy nature. Gambierfluorescein is purified by treating with sulphuric acid, decomposing with sodium hydroxide, and extracting with ether. Its solution becomes red in contact with the air, and, on evaporation, yields a red tar similar to a phlobaphen; this the author names gambier-catechu-red. The fresh alcoholic solution of gambierfluorescein is green by reflected and yellow by transmitted light. Gambierfluorescein, which contains no nitrogen, is insoluble in water and alkalis, but dissolves in acids; the solutions are not fluorescent. When a solution of it, in light petroleum, is cooled, white needles separate, but on drying they turn red and partly lose their crystalline structure. It is contained in the catechu either in the form of a catechin or of a catechutannic acid compound, or in both forms, the compound, which must be analogous in composition to a salt, becoming saponified in the process of extraction. Pegu-catechu does not contain this substance, and the main difference between these catechus is that, whilst gambier-catechu-red is not contained as such in gambier-catechu, pegu-catechu-red is actually contained in pegu-catechu.

Gambier-catechu-red is a reddish-brown, resinous powder, which floats on water, becomes electrified by friction, melts at 130—131°, is insoluble in ether, forms a blood-red solution in sulphuric acid, but neither yields fluorescent solutions nor possesses the basic character of

gambierfluorescein. If a faintly acid solution in alcohol be neutralised with alcholic potassium hydroxide, an intensely dark blue, fluorescent solution is produced, similar to that of tincture of turmeric, but the colour disappears on adding more alkali or on warming. Gambier-catechu-red does not give a precipitate with tannic acid. The acetyl number shows that it still contains hydroxyl groups. The fatty oil obtained from the catechu by means of benzene has an acid number $= 14 \cdot 89$, ether number $= 43 \cdot 33$, and a saponification number $= 58 \cdot 22$; the iodine number is very low. E. W. W.

Colouring Matter of the Red Grape. By LIVIO SOSTEGNI (*Gazzetta*, 1897, **27**, ii, 475—485).—The author has extracted a red colouring matter from a red Italian wine, and also from the œnocyanin of commerce. The colouring matter is precipitated from the œnocyanin by hydrochloric acid and purified by repeatedly precipitating it from alcoholic solution by ether; it is ultimately obtained in amorphous, transparent, red granules, and is readily oxidised by atmospheric oxygen. When dried in a vacuum over sulphuric acid, it has the composition $C_{19}H_{16}O_{10}$, corresponding with Gautier's ampelochroic acid (Abstr., 1892, 1242), but on drying at 150°, it seems to be converted into an *anhydride* of the composition $C_{38}H_{30}O_{19}$. On boiling the substance, $C_{19}H_{16}O_{10}$, in dilute sulphuric acid solution, it is converted into the anhydride, but no pure product could be isolated with more concentrated acid. The colouring matter forms salts with copper, silver, and potassium, but their composition could not be definitely determined; it yields phloroglucinol on heating with aqueous potash, and also combines with bromine. W. J. P.

β-Naphthoquinoline. By ADOLPH CLAUS and HEINRICH BESSELER (*J. pr. chem.*, 1898, [ii], **57**, 49—67).—β-Naphthoquinoline, $\begin{array}{l}CH\text{———}C\text{—}N{:}CH \\ \| \qquad\qquad \| \qquad\quad | \\ CH{\cdot}C_6H_4{\cdot}C{\cdot}CH{:}CH\end{array}$, prepared by Skraup's method (*Monatsh.*, 1883, **4**, 437), crystallises from light petroleum in almost colourless, nacreous leaflets melting at 94° and boiling at 340°. The *methiodide* forms yellow, glistening needles melting and decomposing at 186°; the *methochloride* crystallises from water in colourless needles melting at 138—140°, but if previously dried at 120° does not melt until 236°; the *methodichromate* forms small, yellow needles melting and decomposing at 232°, and the *methosulphate*, prepared by the action of silver sulphate on the methiodide, is excedingly soluble in water, and could not be obtained crystalline.

β-Naphthoquinoline ethobromide, produced when the free base is heated with ethylic bromide in sealed tubes for 3—4 hours at 95°, crystallises from methylic or ethylic alcohol in regular octahedra containing alcohol of crystallisation. From amylic alcohol, it crystallises in colourless needles melting at 238°. The *ethiodide* forms yellow needles melting and decomposing at 206°, and the *ethodichromate* yellow, microscopic needles melting and decomposing at 212°.

β-Naphthoquinoline benzylochloride forms amber-coloured prisms or plates melting at 196°, and the *benzylodichromate* melts at 200°.

All these salts contain water of crystallisation when crystallised from water.

When treated with alkalis in aqueous solution, the alkylated β-naphthoquinolines yield, as do the simple quinolines, quaternary alkylidenequinolinium bases, none of which have been, so far, prepared in a pure condition, but it is hoped that this end may be obtained by repeating the experiments with larger quantities of material.

By the oxidation of the alkylidene bases of β-naphthoquinoline with potassium ferricyanide or mercuric oxide, alkylquinolones are produced. *Methyl-β-naphthoquinolone* separates from alcohol in small, glistening, greenish-yellow crystals melting and decomposing at 183°.

β-Naphthoquinoline methiodide, on treatment with moist silver oxide, gives a strongly basic solution not containing anything soluble in ether and free from iodine, showing that no alkylidene base is formed. This is a striking difference from the simple quinoline derivatives, which, on treatment with moist silver oxide, give the corresponding methylenequinolinium base, readily soluble in ether.

2″-*Bromo-β-naphthoquinoline*, prepared by the Claus-Collischonn method, is readily soluble in alcohol, ether, and chloroform, crystallises in long, silken needles, melts at 117—118°, and sublimes unchanged. On oxidation with chromic acid, it yields β-bromonicotinic acid, thus proving the 2-position of the bromine atom in the pyridine ring. The *methiodide* forms small, yellow needles melting at 225°. Towards alkalis and silver oxide, it behaves like the naphthoquinoline derivatives already mentioned. The *methochloride* melts at 237°.

Nitro-β-naphthoquinoline, obtained as the sole product of nitration of the free base, crystallises from alcohol in yellowish, silky needles melting at 165°. On oxidation with chromic acid, nicotinic acid is produced, showing nitration to have taken place in the naphthalene ring. The *methiodide* forms beautiful, glistening needles, becoming brown on heating to 150°, and melting and decomposing at 210°. The *methochloride* crystallises from alcohol in transparent, glistening plates or prisms melting at 218°.

Amido-β-naphthoquinoline, prepared by the reduction of the above nitro-compound, forms long, yellow crystals melting at 158°, and decomposing on exposure to light. It can be easily diazotised, and on boiling the diazo-sulphate with dilute sulphuric acid, the corresponding *oxy*-compound melting at 208—211° is obtained. The *methiodide* forms garnet-red, glistening plates or prisms melting at 237°, and the *methochloride* small, red crystals melting at 256°. The alkylated nitro- and amido-β-naphthoquinolines show the same behaviour towards alkalis and silver oxide as the alkylated naphthoquinolines. This will be dealt with more fully later. A. W. C.

α-Naphthoquinoline. By Adolph Claus and Paul Imhoff (*J. pr. chem.*, 1898, [ii], 57, 68—84).—*α-Naphthoquinoline*,

$$\begin{array}{l} \mathrm{CH{\text{———}}C{\cdot}CH{:}CH} \\ \mathrm{CH{\cdot}C_6H_4{\cdot}C{—}N{:}CH} \end{array}.$$

The preparation of this substance by Skraup's method presents especial difficulties. It is a pleasant smelling base readily soluble in the ordinary organic solvents, crystallises from alcohol in colourless leaflets melting at 51° and boiling at 338° (uncorr.), and decomposes much more readily than β-naphthoquinoline. The *hydrochloride* forms

small, colourless needles melting at 213°; the *disulphate* crystallises from alcohol in glistening plates or prisms melting at 213°; the *nitrate* forms beautiful, silky needles melting at 135—137°; the *dichromate* yellow, glistening plates decomposing at 130°; and the *platinochloride* small, yellow needles melting and decomposing at 224°.

a-Naphthoquinoline methiodide, obtained by heating the components for 5 hours at 115° in sealed tubes, crystallises from water or alcohol in beautiful, golden-yellow, glistening plates or needles melting at 179°; the *methochloride* forms colourless, prismatic needles melting at 133°; the *methodichromate* crystallises from water in orange-red, glistening needles decomposing at 190°, and the *methosulphate* in small, white needles melting at 162°.

On hydrolysis with alkalis, the alkylated α-naphthoquinolines are quantitatively converted into the methylene-α-naphthoquinolinium, but with moist silver oxide a substance is produced readily soluble in ether, thus showing a marked difference from the similar α-naphthoquinoline derivatives, probably due to a difference in constitution. The reaction is, however, very complicated, and before a satisfactory explanation is forthcoming, it must be much more fully studied.

Methyl-a-naphthoquinolone prepared by the oxidation of α-naphthoquinoline methiodide with mercuric oxide or potassium ferrocyanide in alkaline solution, crystallises from alcohol in glistening needles possessing a peculiar green colour and melting at 175°. It is not acted on by hot or cold dilute hydrochloric acid, but is dissolved by the concentrated acid, and yields a *platinochloride* which melts and decomposes at 262°.

a-Naphthoquinoline-3′-sulphonic acid, $\begin{matrix} C(SO_3H)\cdot C\cdot CH{:}CH \\ \| \qquad\quad \| \qquad\quad | \\ CH\cdot C_6H_4\cdot C—N{:}CH \end{matrix}$, obtained by the action of fuming sulphuric acid on the free base, forms beautiful, white crystals. Neither the acid nor its *potassium, sodium, barium*, or *silver* salt melts below 300°. The *methylic* salt separates from alcohol in small, colourless needles melting at 127°.

a-Naphthoquinoline-3′-sulphonic chloride forms yellow crystals melting at 116°. This substance which the authors propose to further investi gate, was converted in the ordinary way into the *sulphonamide*, which forms small, glistening, colourless prisms melting at 225°.

3′-Hydroxy-a-naphthoquinoline, obtained by fusing the sulphonic acid with potash, crystallises from alcohol in glistening needles showing no sharp melting point; it blackens when heated to 240°, and melts and decomposes about 270°. The *hydrochloride* forms glistening, orange-yellow needles.

On nitration, α-naphthoquinoline yields two isomeric *mononitro*-derivatives in which the nitro-groups are in positions 3′ and 4′ respectively. The one crystallises in colourless needles melting at 151°, the other in yellow needles melting at 138°. Both yield nitrates melting respectively at 178° and 173°. A. W. C.

Structural Relationships of the Two Naphthoquinolines. By ADOLPH CLAUS (*J. pr. chem.*, 1898, [ii], 57, 85—94).—In discussing at some length the probable constitution of the isomeric naphthoquinolines, the author points out that whereas Kekulé's benzene configura-

tion shows only one possible difference, namely, that the nitrogen atom of the pyridine ring is combined with different carbon atoms of the naphthalene ring, the "central" benzene formula allows a second and more substantial difference depending on the distribution of the central bonds. That some such important difference does exist seems probable from the varied behaviour of the naphthoquinolines on oxidation with chromic acid, and of their alkylated derivatives on treatment with alkalis or silver oxide.

The further study of this problem affords an opportunity for testing the efficacy of the central formula, of which the author proposes to take advantage. A. W. C.

Relationship of Safranines, Isorosindulines, and Rosindulines. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1898, **31**, 299—308. Compare Abstr., 1897, i, 636).—The authors have shown (*loc. cit.*) that rosindone and aposafranine are converted by phosphorus pentachloride into chloronapththophenazonium chloride and chlorophenylphenazonium chloride respectively. The change is now found to be a general one for the indones of this series.

Dichlorophenylphenazonium chloride, $C_6H_3Cl<{N \atop NPhCl}>C_6H_3Cl$, [N : N : Cl : Cl = 1 : 2 : 4 : 4], is obtained by dissolving safranol in five times its weight of phosphorus oxychloride, and treating it with phosphorus pentachloride (2 mols.); it crystallises from alcohol in reddish-yellow needles which exhibit a bluish reflex. The *nitrate* crystallises in steel-blue leaflets, and the *aurochloride* forms golden leaflets. When the aqueous solution is boiled with sodium acetate, *chloraposafranone*, $O<{C_6H_3:N \atop NPh}>C_6H_3Cl$, is produced; it crystallises from alcohol in brown prisms with bronze reflex. *Chlorophenylaposafranine,*

$$NHPh\cdot C_6H_3<{N \atop NPhCl}>C_6H_3Cl,$$

obtained by treating an alcoholic solution of dichlorophenylphenazonium chloride with aniline, crystallises from water in highly lustrous, yellow needles, and forms a green solution in concentrated sulphuric acid. The *platinochloride* is almost black, and has a metallic lustre.

Chlorophenylnapththophenazonium chloride, $C_6H_3Cl<{N \atop NPhCl}>C_{10}H_6$, is obtained from isorosindone, phosphorus oxychloride, and phosphorus pentachloride; it crystallises from a mixture of alcohol and ether in long, brownish-yellow needles, and separates from water with $1H_2O$. The *bromide* forms brownish-red, lustrous plates, and the *iodide* is dark-green; the *nitrate* crystallises in brown plates, the *platinochloride* separates from hot water in slender, brick-red needles, and the *aurochloride* is also red. Aniline converts the alcoholic solution of the chloride into phenylisorosinduline hydrochloride.

Methylic bromide converts phenylrosinduline at 100° into a methobromide which is resolved by alcoholic potash into rosindone and methylaniline. Phenylisorosinduline, on the other hand, yields a

methobromide, which is converted first into an unstable hydrate; the latter then undergoes oxidation into methylanilidorosindone.

Isorosindone *methiodide* crystallises from alcohol in lustrous needles, and loses methylic iodide at 170—180°. The *platinochloride* crystallises in reddish-brown needles, and the *aurochloride* forms red needles; the nitrate crystallises in leaflets having a green lustre, and becomes red when powdered. Alcoholic potash regenerates isorosindone from the methiodide, and also gives rise to *methoxyrosindone*, $O<\begin{matrix}C_{10}H_5{:}N\\ | \\ NPh\text{——}\end{matrix}>C_6H_3\cdot OMe$, which crystallises from a mixture of benzene and alcohol in reddish-brown leaflets containing benzene, and melts at 264—265°; the *methiodide* separates from alcohol in brown crystals having a green reflex. Concentrated sulphuric acid at 170° converts methoxyrosindone into hydroxyrosindone. M. O. F.

3-Hydroxy-1 : 2 : 4-triazole and Acidylsemicarbazides. By OSKAR WIDMAN and ASTRID CLEVE (*Ber.*, 1898, **31**, 378—381).—*Diformylsemicarbazide*, $N(CHO)_2\cdot NH\cdot CO\cdot NH_2$, is obtained when acetonesemicarbazone is boiled for some 4 hours with a large excess of the strongest formic acid (sp. gr. = 1·23). After the excess of formic acid has been distilled off, the product is crystallised from alcohol, when it forms colourless prisms melting at 158°, readily soluble in alcohol or water, but insoluble in ether. It gives a bluish-green precipitate with Fehling's solution but does not reduce it.

3-*Hydroxy*-1 : 2 : 4-*triazole*, $\begin{matrix}CH{:}N\\ | \\ NH\cdot N\end{matrix}\!\!>C\cdot OH$, is formed when acetonesemicarbazone is boiled for about 8 hours with a smaller quantity of concentrated formic acid; the residue, after the greater part of the formic acid has been distilled off, is cooled and rubbed with a small quantity of alcohol, when it yields crystals of the triazole; this melts at 234°, is readily soluble in alcohol or water, but insoluble in ether, and has acid but not basic properties. Its *silver* salt, $C_2HN_3OAg_2$, *basic copper* salt, $O(Cu\cdot O\cdot C_2H_2N_3)_2 + H_2O$, and *diacetyl* derivative crystallising in needles and melting at 137° are described.

Acetylsemicarbazide, $NHAc\cdot NH\cdot CO\cdot NH_2$, is obtained when finely powdered, free semicarbazide is warmed on the water bath with acetic anhydride until all has dissolved. On the addition of alcohol, the acetyl derivative crystallises in small, hard, nodular masses; it melts at 165°, and is soluble in ether. *Isobutyrylsemicarbazide* melts at 163° and *benzoylsemicarbazide* crystallises in rhombic plates melting at 225°. These compounds cannot be converted into triazoles on account of the ease with which they are hydrolysed. The acetyl compound is hydrolysed by boiling with water, and the others when boiled with acids or alkalis. J. J. S.

Methyldioxytriazine. By ADRIANO OSTROGOVICH (*Gazzetta*, 1897, **27**, ii, 416—429).—The author has previously shown (Abstr., 1896, i, 261, 393) that methyldioxytriazine is formed on heating acetylurethane with carbamide. It is now shown that acetylcarbamide, acetylbiuret, and cyanuric acid are formed at the same time; on heating acetylcarb-

amide with urethane at 180—185°, methyldioxytriazine, acetylbiuret, and cyanuric acid are also obtained.

Acetylbiuret, on treatment with potash in alcoholic solution, yields a *potassium* derivative, $NHAc\cdot CO\cdot NH\cdot CO\cdot NH_2,KOH$, which crystallises in colourless needles; it is soluble in boiling alcohol but partially hydrolyses, giving potassium acetate and biuret; the corresponding *sodium* compound was prepared. By the action of sodium ethoxide on an alcoholic solution of acetylbiuret, a *substance* of the composition $NHAc\cdot CO\cdot NH\cdot CO\cdot NH_2,EtONa$, is obtained as a white, crystalline powder.

Methylic methyldioxytriazine, $NH{<}{\begin{smallmatrix}CMe=N\\ CO\cdot NMe\end{smallmatrix}}{>}CO$, obtained by heating the silver derivative of methyldioxytriazine with methylic iodide and methylic alcohol in a closed tube at 100°, crystallises with $1H_2O$ in minute, white crystals and is hydrolysed by potash with formation of methylamine. It was not obtained by heating acetylurethane with methylcarbamide at 140—145°, but methylacetylcarbamide was formed.

Ethylic methyldioxytriazine, $C_6H_9N_3O_2$, is obtained by the action of ethylic iodide on methyldioxytriazine at ordinary temperatures; it forms minute, white crystals, and yields ethylamine on hydrolysis with potash.

On treating acetylbiuret with acetic chloride, reaction occurs in accordance with the equation $C_2H_4AcN_3O_2 + 2AcCl = HCl + CO_2 + AcOH + C_3HMe_2N_3O,HCl$, *dimethyloxytriazine hydrochloride* being produced; this crystallises in needles, is very soluble in water, and forms a *platinochloride* which crystallises in large, yellow prisms. The free *base*, $C_5H_7N_3O + H_2O$, is obtained in large prisms and the *sulphate* crystallises either anhydrous or with $1H_2O$. The *sodium* salt $C_5H_6N_3ONa + 2H_2O$, and the *barium* salt, $(C_5H_6N_3O)_2Ba + 7H_2O$, crystallise in colourless needles. On treating a solution of the base or one of its compounds with bromine, a *compound*, $C_5H_4Br_3N_3O + H_2O$, crystallising in white scales, is obtained. W. J. P.

Methods of Formation of Paranitrodiphenyltetrazole. By EDGAR WEDEKIND (*Ber.*, 1898, **31**, 473—479. Compare Abstr., 1896, i, 630).—Paranitrodiphenyltetrazole, $NO_2\cdot C_6H_4\cdot C{<}{\begin{smallmatrix}N\cdot NPh\\ N:N\end{smallmatrix}}$, can be prepared by the following methods.

I.—When alcoholic solutions of nitrobenzylidenehydrazone and diazoparanisidine chloride are mixed, *paranitroparamethoxyformazylbenzene*, $NHPh\cdot N:C(C_6H_4\cdot NO_2)\cdot N:N\cdot C_6H_4\cdot OMe$, is produced in lustrous, brown needles which melt at 199° and form a deep green solution in sulphuric acid. When this compound is treated in chloroform solution with alcoholic hydrogen chloride and nitrous acid, it forms a *chloride* which does not crystallise, but yields, with potassium iodide, a yellow precipitate of *paranitroparamethoxytriphenyltetrazolium iodide*, $NO_2\cdot C_6H_4\cdot C{<}{\begin{smallmatrix}N\cdot NPh\\ N:NI\cdot C_6H_4\cdot OMe\end{smallmatrix}}$, which softens at 139—140°, melts at 166—168°, and is sparingly soluble in most solvents. The impure chloride is converted by fuming nitric acid at 140—150°, into

paranitroparahydroxytriphenyltetrazolium chloride,

$$NO_2\cdot C_6H_4\cdot C{<}{N\cdot NPh \atop N:NCl\cdot C_6H_4\cdot OH},$$

which crystallises in pale yellow needles, melts at 208—209°, and decomposes at 233°. When this compound is converted into the *nitrate*, by precipitation with silver nitrate, and then oxidised by potassium permanganate in acid solution, it yields *paranitrodiphenyltetrazole* as a white, crystalline powder melting at 199—200°.

II.—The same nitrotetrazole can be obtained more readily by treating paranitroguanazylbenzene with concentrated nitric acid at 30—40°.

Paranitroparahydroxyformazylbenzene,

$$NHPh\cdot N:C(C_6H_4\cdot NO_2)\cdot N:N\cdot C_6H_4\cdot OH,$$

obtained when the nitrohydroxytriphenyltetrazolium chloride described above is reduced by ammonium sulphide, forms slender, brownish-red, matted needles melting at 194°.

When paranitrobenzylideneamidoguanidine is treated with nitric acid in a similar manner to paranitroguanazylbenzene, it yields a substance which is probably a *dinitrobenzylideneamidoguanidine*, $C_8N_6H_8O_4$; this crystallises in yellow needles melting at 248—249°.

A. H.

New Method of Preparing Tetrazine Derivatives. By ALFRED JUNGHAHN (*Ber.*, 1898, **31**, 312—313. Compare Pinner, this vol., i, 94).—Tetrazine derivatives are formed by the action of hydrazine on thiamides. The amide is dissolved in alcohol and heated with aqueous hydrazine in a reflux apparatus during 1 hour. M. O. F.

Azimido-derivatives of Benzimidazoles. By STEFAN VON NIEMENTOWSKI (*Ber.*, 1898, **31**, 314—323. Compare this vol., i, 210).—The *azimide* of β-orthamidophenylbenzimidazole,

$$C_6H_4{<}{N:C \atop N\cdot N:N}{>}C_6H_4,$$

is obtained in quantitative yield on adding alkali nitrite to an alcoholic solution of orthamidobenzimidazole acidified with hydrochloric acid, or by warming a neutral, alcoholic solution of the imidazole with amylic nitrite. It crystallises from alcohol in bright yellow, lustrous needles, and melts at 207—208°. The *hydrochloride* melts and intumesces at 200°, and the *aurochloride* contains $2H_2O$ and melts at 220°.

The *azimide* of β-orthamidophenylmetatolimidazole,

$$\begin{array}{l} N{=\!=}C\cdot C_6H_4 \\ C_6H_3Me\cdot N{-}N \end{array}{>}N,$$

crystallises in yellow needles and melts at 187—188°.

β-Orthohydroxyphenylmetatolimidazole, $C_6H_3Me{<}{N \atop NH}{>}C\cdot C_6H_4\cdot OH$, is obtained by hydrolysing the foregoing azimide with dilute sulphuric acid; it crystallises from alcohol in needles and melts at 241°.

The *azimide* of β-orthamidoparatolylbenzimidazole,

$$\begin{array}{l} N{=\!=}C\cdot C_6H_3Me \\ C_6H_4\cdot N{-}N \end{array}{>}N,$$

crystallises in yellow needles and melts at 185°; exposure to sunlight renders it darker. The *platinochloride* crystallises in brown leaflets, softens at 275°, but is not melted at 290°.

The *azimide* of β-orthamidoparatolyltolimidazole,

$$\begin{array}{l} N\!=\!=\!=\!C\cdot C_6H_3Me \\ \quad | \qquad\quad | \\ C_6H_3Me\cdot N\!-\!-\!N \end{array}\!\!>\!N,$$

crystallises in bright yellow needles and melts at 197°.

When the azimide of β-orthamidophenylbenzimidazole is dissolved in glacial acetic acid and treated with bromine (2 mols.), it yields the *dibromide*, $C_{13}H_8N_4Br_2$, which melts at 112°. There are also formed two isomeric monobromo-derivatives, the *monobromide*, $C_{13}H_7N_4Br$, which crystallises in pale orange needles and melts at 131—132°, and the more readily soluble *monobromide*, which crystallises in slender, dark yellow needles and melts at 146°.

The azimide of β-orthamidoparatolylbenzimidazole yields the *pentabromide*, $C_{14}H_7N_4Br_5$, which melts and decomposes at 120—130°; ammonia converts it into the *dibromide*, $C_{14}H_8N_4Br_2$, which crystallises from glacial acetic acid in straw-yellow leaflets, and melts at 257°.

The azimide of β-orthamidoparatolylmetatolimidazole yields the *pentabromide*, $C_{15}H_{11}N_4Br_5$, which melts and decomposes at 155°; the *monobromide* melts at 254°.

β-Naphthol-β-orthazobromophenylbenzimidazole, $C_{23}H_{15}N_4OBr$, crystallises in red needles and melts at 160—170°. The *hydrochloride* crystallises from glacial acetic acid, and melts and decomposes at about 252°; the solution in concentrated sulphuric acid is deep cherry red.

The *hydrochloride* of β-naphthol-β-orthazoparatolylbenzimidazole forms a deep red, crystalline mass, and melts and decomposes at 276°.

β-Naphthol-β-orthazoparatolylmetatolimidazole has not been obtained in a condition free from β-naphthol; it melts at 147—150°.

M. O. F.

2-Methyldihydropyrroline, 1 : 2-Dimethyldihydropyrroline, and 1 : 2-Dimethylpyrrolidine. By R. Hielscher (*Ber.*, 1898, **31**, 277—280).—*2-Methyldihydropyrroline*, $NH<\begin{matrix}CMe\!:\!CH \\ CH_2\cdot CH_2\end{matrix}$, obtained by the action of alcoholic ammonia at 40—45° on methyl γ-bromopropyl ketone, boils at 50—51° under 110—116 mm. pressure, and has a sp. gr. = 0·8995 at 22°; the *aurochloride* and *platinochloride* melt at 108° and 141—142° respectively; the hydrochloride is deliquescent. With methylamine instead of ammonia, reaction ensues at 0°; the product, 1 : 2-*dimethyldihydropyrroline*, boils at 53—54° under 93—96 mm. pressure, and has sp. gr. = 0·9333 at 22°; the *aurochloride* and *platinochloride* melt and decompose at 159° and 172—173° respectively. The base itself can be reduced by tin and hydrochloric acid to 1 : 2-*dimethylpyrrolidine*, which boils at 87—88·5°, and has a sp. gr. = 0·8299 at 20°; the *aurochloride* melts at 179—180°, whilst the platinochloride was only obtained as a syrup.

C. F. B.

Isomerism in the Piperidine Series. By Albert Ladenburg (*Ber.*, 1898, **31**, 286—289).—The compound obtained by Lipp (Abstr., 1892, 1244, and *Annalen*, **289**, 173) by allowing methylamine to react

with the bromide of acetobutylic alcohol and adding formaldehyde to the product, and formulated by him as 1-methyl-2-hydroxyethyl-Δ^2-tetrahydropyridine, (I),

I. (Lipp).	II. (Ladenburg).	III.
$CH_2{\cdot}CH_2{\cdot}CH$	$CH_2{\cdot}CH_2{\cdot}C{\cdot}CH_2{\cdot}OH$	$CH_2{\cdot}CH_2{\cdot}C{\cdot}CH_2$
$CH_2{\cdot}NMe{\cdot}C{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	$CH_2{\cdot}NMe{\cdot}C{\cdot}CH_3$	$CH_2{\cdot}NMe{\cdot}C{\cdot}CH_2$

must rather have the constitution II. For when this compound is made to lose water, the product, which, presumably, has the constitution III, takes up 2 atoms of hydrogen, and then, when heated with hydrochloric acid, loses methyl and yields, not 2-, but 3-ethylpiperidine.

C. F. B.

2-Ethylpiperidine and its Methyl Derivative. By ALBERT LADENBURG (*Ber.*, 1898, **31**, 290—291).—2-Ethylpiperidine has been prepared in a purer state than hitherto by the reduction, with sodium and alcohol, of 2-ethylpyridine which had been purified by repeated crystallisation of the mercurochloride (the aurochloride gives better results). It boils at 141—143°, and has a sp. gr. = 0·8666 at 0°; the hydrochloride melts at 178—181°, the platinochloride at 189°, decomposing at 191°, and the yellow *aurochloride*, previously obtained as an oil only, at 129—130°.

The methyl derivative was prepared by heating it with potassium methylic sulphate in aqueous alcoholic solution on the water bath, and removing unchanged secondary base in the form of its nitrosamine. It boils at 150—151·5°, and has a sp. gr. = 0·8515 at 0°; the *aurochloride* melts at 122—123°; the mercurochloride and deliquescent hydrochloride were also obtained crystallised, but not the platinochloride.

C. F. B.

1-Methylpipecoline (1 : 2-Dimethylpiperidine). By ALBERT LADENBURG (*Ber.*, 1898, **31**, 291—292).—This substance has been prepared by reducing picoline (2-methylpyridine) and methylating the product with potassium methylic sulphate, the unchanged secondary base being removed as the nitrosamine, and it has been compared with Lipp's 1-methylpipecolylalkine (Abstr., 1892, 1244, and *Annalen*, 1895, **289**, 226), obtained by acting with methylamine on acetobutylic alcohol, and reducing the product; the two substances are identical. The boiling point is 127·9° (corr.); the platinochloride, aurochloride, picrate, and stannochloride melt at 183—184°, 199—201°, 235—236°, and 129—130° respectively; the platinochloride of the methochloride melts and decomposes at 222°, and its *aurochloride* melts at 258°.

C. F. B.

Synthesis of Xanthine from Hydrogen Cyanide. By ARMAND GAUTIER (*Ber.*, 1898, **31**, 449—450).—The substance formerly obtained by the author from hydrocyanic acid, and characterised by him as xanthine, shows a number of reactions, which are all given, not only by natural xanthine, but also by other members of the same group of compounds. In view of E. Fischer's statement (this vol., i, 214) that the compound obtained by him from hydrocyanic acid does not show the murexide reaction, and is therefore not identical with xanthine, the author proposes to reinvestigate the reaction, and

especially the other products which accompany the compound, which he has termed xanthine.

A. H.

An Apparent Intramolecular Rearrangement in the Purine Group. By EMIL FISCHER (*Ber.*, 1898, 31, 542—545).—2-Chloro-6-amido-7-methylpurine (this vol., i, 280), when warmed with dilute aqueous alkali, is decomposed, yielding 7-methylguanine,

$$\begin{array}{l}NH\cdot CO\cdot C\cdot NMe \\ NH_2\cdot C:N——C——N\end{array}\!\!>\!CH, \text{ and not } \begin{array}{l}N:C(NH_2)\cdot C\cdot NMe \\ CO\cdot NH——C——N\end{array}\!\!>\!CH,$$

an amido-oxymethylpurine, as would be expected if the reaction were a normal one. It was at first thought possible that a migration of the amido-group had taken place, but it has since been proved to be probable that the ring is first broken between N_1 and C_6 by the addition of the elements of a molecule of water, and then again closed by the elimination of a molecule of hydrogen chloride.

2-Chloro-6-methylamido-7-methylpurine is also decomposed by aqueous alkalis, yielding the dimethylguanine, $\begin{array}{l}NMe\cdot CO\cdot C\cdot NMe \\ C(NH_2):N\cdot C——N\end{array}\!\!>\!CH$ (this vol., i, 98).

J. J. S.

Thiopurines. By EMIL FISCHER (*Ber.*, 1898, 31, 431—446).—When 2 : 6-dichloro-7-methylpurine is shaken for a quarter of an hour or so with normal potassium hydrosulphide solution in the cold, reaction takes place more readily than with potassium hydroxide, and the product is 2-*chloro*-6-*thio*-7-*methylpurine*, $\begin{array}{l}N:C(SH)\cdot C\cdot NMe \\ CCl:N——C——N\end{array}\!\!>\!CH,$ which is formulated as containing the group $:C(SH)\cdot$ rather than $\cdot CS\cdot$, because its methylic derivative (see below) readily yields methylic hydrosulphide when boiled with acids. This substance has no definite melting point; it is acid in character, like most of the substances described in the present paper, and forms many salts; it is oxidised by hydrochloric acid and potassium chlorate, or by alkaline hypobromites, but the product gives no murexide reaction; heating with strong hydrochloric acid displaces the Cl by OH, but removes some of the sulphur at the same time; reduction with hydriodic acid (sp. gr. = 1·96) and phosphonium iodide converts it into 6-*thio*-7-*methylpurine*, which crystallises with $1H_2O$ and melts when anhydrous at 310—311° (corr.). When this substance is shaken with methylic iodide and normal potash solution, it yields 6-methylthio-7-methylpurine, which melts at 212—213° (corr.) (in the case of the oxypurines, the methyl usually goes to the nitrogen atom); when it is heated with nitric acid of sp. gr. = 1·16, it is oxidised to 6-oxy-7-methylpurine. When 2-chloro-6-thio-7-methylpurine is heated with alcoholic sodium ethoxide at 100°, it forms 2-*ethoxy*-6-*thio*-7-*methylpurine*; this melts at 234° (corr.), forming a new substance, which then decomposes at 270—280°; heated on the water bath with hydrochloric acid of sp. gr. = 1·19, it yields 2-*oxy*-6-*thio*-7-*methylpurine*, which crystallises with $1H_2O$, and melts and decomposes at 343° (corr.) when anhydrous.

When 2 : 6-dichloro-7-methylpurine is treated with excess of aqueous potassium hydrosulphide at 100° instead of at the ordinary tem-

perature, both chlorine atoms are removed, and 2 : 6-*dithio*-7-*methylpurine*, which has no definite melting point, is formed.

When 2 : 6 : 8-trichloro-7-methylpurine (1 mol.) is shaken for $2\frac{1}{2}$ hours with normal aqueous potassium hydrosulphide ($1\frac{1}{2}$ mols.), the product contains some dithiomethylpurine, but consists for the most part of monothio-compounds. On reducing it with hydriodic acid and phosphonium iodide, finally on the water bath, the hydriodide of 6-thio-7-methylpurine separates out first, accompanied by the hydriodide of the dithio-compound; these can be separated by decomposing the hydriodides with ammonia, evaporating, and extracting the residue with water, in which the monothio-compound is less soluble. The mother liquor from the hydriodides contains another thiomethylpurine, probably 8-*thio*-7-*methylpurine*, which melts at 248—249° (corr.). Potassium hydrosulphide, then, attacks trichloro-7-methylpurine chiefly in the 6-position; with potassium hydroxide, it is almost entirely the 8-chlorine atom that is removed.

When trichloro-7-methylpurine is heated with excess of aqueous potassium hydrosulphide at 100°, the product is *trithio*-7-*methylpurine*, which is yellow, crystallises with $1H_2O$, and has no definite melting point.

By heating trichloropurine itself with a large excess of aqueous potassium hydrosulphide at 100°, *trithiopurine*, the sulphur analogue of uric acid, is obtained; this is yellow, and has no definite melting point.

Bromoxanthine, which will not react with potassium hydroxide, is converted by a large excess of aqueous potassium hydrosulphide at 120° into yellowish 2 : 6-*dioxy*-8-*thiopurine*; this crystallises with $1H_2O$, and, when heated, decomposes without melting.

C. F. B.

Diascorine, the Alkaloid obtained from the Tuber of Diascorea Hirsuta Bl. By H. W. Schütte (*Chem. Centr.*, 1897, ii, 130—131; from *Ned. Tijdschr. Pharm.*, 9, 131—143).—Diascorine was discovered by Boorsma in the tuber of *Diascorea hirsuta Bl.*, which is known as "gadoeng" in Java. The alkaloid, which is extracted from the tuber by a solution of hydrogen chloride in alcohol, crystallises in yellowish-green plates, has a bitter taste, melts at 43·5° (uncorr.), is very hygroscopic, and easily soluble in water, alcohol, acetone, and chloroform, slightly in ether and benzene, and very slightly in light petroleum; it is a strong base, and slightly volatile in steam. With sulphuric acid and potassium iodate, it gives a brownish-yellow coloration which rapidly becomes bluish-violet; with sodium nitroprusside and an alkali, a reddish-violet coloration; and on warming with sulphuric acid, a reddish-violet. With mercuric chloride solution, it gives a white, amorphous precipitate, and with picric acid a yellow precipitate which melts at 184°; with a solution of iodine in potassium iodide, it forms a white, amorphous precipitate, and with Bouchardat's reagent a brown precipitate, which gradually disappears. Phosphotungstic acid gives a white precipitate; phosphomolybdic acid, a yellowish-white; potassium cadmium iodide, a white; potassium bismuth iodide, a red, and bromine water a transient, yellow precipitate. The *hydro-*

chloride, $C_{13}H_{19}NO_2,HCl + 2H_2O$, crystallises from absolute alcohol in needles or plates, is very easily soluble in water, and has a specific rotatory power $[\alpha]_D = +4° 40'$; the refractive index of a solution of 1·75 grams in 100 grams of water $n_D = 1·33776$. It loses its water of crystallisation at 100°, and the anhydrous salt melts at 204° (uncorr.). The *platinochloride* crystallises with $3H_2O$ in orange-yellow plates, and the anhydrous salt melts and intumesces at 199—200°. The *aurochloride* crystallises with $\frac{1}{4}H_2O$ in yellow needles, the anhydrous salt melting at 171°. Diascorine has a weaker, but a similar, physiological effect to that of picrotoxin.

Boorsma's diascorine and diascorecine are identical, and diascorine is the only poisonous base contained in the tuber. E. W. W.

Formulæ of Proteids and Composition and Nature of the Melanins. By OSWALD SCHMIEDEBERG (*Chem. Centr.*, 1897, i, 1062—1064; from *Arch. expt. Path. Pharm.*, **39**, 1—84).—The dark brown to black pigments known as melanins are supposed to be either independent compounds like hæmoglobin, or derivatives of proteids, and the author, after examining a melanotic sarcoma, is inclined to the latter view. In order to readily compare the composition of these substances with that of other such compounds, he has calculated empirical formulæ from the various quoted analyses, with the following results. Fibrin, $C_{108}H_{162}N_{30}SO_{34}$; fibrinoglobulin, $C_{114}H_{176}N_{30}SO_{37}$; fibrinogen, $C_{111}H_{168}N_{30}SO_{35}$; paraglobulin from cows' or horses' blood, $C_{117}H_{182}N_{30}SO_{38} + \frac{1}{2}H_2O$; protofibrinose (protalbumose from fibrin), heterofibrinose, deuteroalbumose from Witte's peptone, which the author names deuterofibrinose, the hemialbumoses (with varying amounts of water of crystallisation according to Kühne and Chittenden's analyses), $C_{102}H_{150}N_{30}SO_{31}$; dysofibrinose, $C_{105}H_{156}N_{30}SO_{33} + 4H_2O$; amphopeptone, $C_{108}H_{178}N_{30}SO_{43}$; antipeptone, $C_{108}H_{178}N_{30}SO_{43} + 1\frac{1}{2}H_2O$ (the author attributes the varying composition of the different preparations to the existence of several antipeptones, which differ from one another in the number of leucine or tyrosine molecules they have lost); Kühne and Chittenden's albumoses from paraglobulin—protalbumose, $C_{111}H_{176}N_{30}SO_{38} + \frac{1}{2}H_2O$; heteroalbumose, $C_{114}H_{176}N_{30}SO_{38} + \frac{1}{2}H_2O$; deuteroalbumose, $C_{111}H_{176}N_{30}SO_{38} + H_2O$; Kühne's myosin, $C_{108}H_{172}N_{30}SO_{33}$; myoglobulin, $C_{114}H_{174}N_{30}SO_{36} + \frac{1}{2}H_2O$; protalbumose from myosin, $C_{108}H_{174}N_{30}SO_{34}$; deuteroalbumose from myosin,

$$C_{105}H_{178}N_{30}SO_{36};$$

serum albumin from horses' blood, $C_{78}H_{122}N_{20}SO_{24}$; egg-albumin, $C_{80}H_{122}N_{20}SO_{24} + H_2O$; Kühne's antialbumide, $C_{120}H_{187}N_{27}SO_{37}$; hemipeptone obtained from serum albumin by boiling with 0·5 per cent. sulphuric acid, $C_{111}H_{176}N_{30}SO_{44} + \frac{1}{2}H_2O$; Lieberkuhn's deamidoalbuminic acid, $C_{160}H_{239}N_{27}S_2O_{65}$; Maly's oxyprotosulphonic acid,

$$C_{80}H_{122}N_{20}SO_{27} + 2\tfrac{1}{2}H_2O.$$

Melanoidic acid, $C_{240}H_{23}N_{17}S_2O_{58}$, is prepared from serum albumin, purified by Hofmeister's method with ammonium sulphate, by coagulating and then digesting with dilute hydrochloric acid. It is a black, friable mass, and is only very slightly soluble in potassium hydroxide solution.

To prepare the melanin, the swellings from a large sarcomatous liver were macerated, washed with water, filtered, the fats then removed by

alcohol and ether, and the residue finally digested with pepsin-hydrochloric acid. The pigment grains remained undissolved, and were purified by warming with very dilute potassium hydroxide solution at 50—60° and filtering. The grains which pass through the paper were washed and dried in a centrifugal machine. Neglecting the 2·7 per cent. of iron which the melanin contained, its composition corresponded with the formula $C_{68}H_{72}N_{10}SO_{26} + \frac{1}{2}H_2O$.

Sarcomelaninic acid was prepared by digesting the pigment grains with dilute potassium hydroxide solution on the water bath for 2 or 3 days, and then precipitating with hydrochloric acid; this acid is not precipitated by acetic acid. Analyses of two preparations corresponded with the empirical formulæ $C_{68}H_{64}N_{10}SO_{26} + 2\frac{1}{2}H_2O$ and $C_{68}H_{67}N_{13}SO_{26} + 3\frac{1}{2}H_2O$ respectively.

The melanins hitherto prepared have very various compositions, thus the composition of Nencki's hippomelanin, prepared from the melanotic sarcomata of a horse, corresponds with the formula $C_{52}H_{39}N_9SO_{18} + \frac{1}{2}H_2O$, his phymatorhusin from human spleen and liver sarcomata with $C_{24}H_{20}N_4S_2O_7$, and Mörner's melanin with $C_{36}H_{43}N_7S_2O_7 + 1\frac{1}{2}H_2O$. Although in many cases the substances analysed were not homogeneous compounds, still the author maintains that this difference in composition is due to the different manner of their origin from proteids.

E. W. W

Prevention of the Precipitation of certain Proteids by Metallic Silver. By H. Schadee van der Does (*Zeit. physiol. Chem.*, 1898, **24**, 351—353).—If fresh white of egg or blood-serum is shaken with freshly precipitated silver (0·05 grams to 10 c.c.) for a minute and then filtered, the filtrate is not coagulable by heat, neither are the globulins precipitated on dilution with water. The filtrate contains silver, and the silver on the filter paper contains something else, probably sulphur. The peculiarity in the behaviour of the proteid solutions may be due to the presence of silver in combination, or to the removal of something (? sulphur) from the proteid by the silver. The solutions resist putrefaction for a long time.

W. D. H.

[Decomposition of Albumin by Hydrochloric Acid]. By Rudolf Cohn (*Zeit. physiol. Chem.*, 1898, **24**, 358—359).—Panzer (*ibid.*, 138) states that glutamic acid is obtainable in large quantities from the decomposition of proteid by hydrochloric acid. The present author states that he also has now found this to be the case, contrary to what he stated in his first contribution to the subject (Abstr., 1896, i, 658).

W. D. H.

Preparation of a Carbohydrate from Egg-albumin. By John G. Spenzer (*Zeit. physiol. Chem.*, 1898, **24**, 354—357).—It is quite easy to prepare a carbohydrate from white of egg as Schützenberger, and, later, Pavy showed. The present paper states that this originates from the ovo-mucoid, and that if egg-albumin is obtained free from that substance it yields no carbohydrate at all.

W. D. H.

Urobilin. By GEORGES DENIGÉS (*Chem. Centr.*, 1897, i, 1128—1129; from *Bull. Soc. Pharm. Bordeaux*, 1897, März).—When ammonia is added to a solution of urobilin, its red colour changes to yellow and the absorption band in the blue portion of the spectrum disappears, but when a soluble zinc salt is added to the ammoniacal solution, this band reappears in a position nearer the red end of the spectrum and the solution shows a characteristic green fluorescence. The ammoniacal solution of urobilin gives a reddish coloration with mercuric sulphate, although the mixture is strongly alkaline, and nickel and copper salts give a violet coloration similar to that of the biuret reaction. Silver, ferric, ferrous and manganous salts (in presence of glycerol to avoid precipitation) and cadmium and magnesium salts have no effect. Thus the active salts are those which easily form double salts with ammonia or stable amine-like derivatives.

The presence of urobilin in highly coloured urines is difficult to detect by the spectroscope, especially when the colour is caused by bile pigments which absorb all the rays from yellow to violet, and although these colouring matters may be removed by lead or mercuric acetate, urobilin is also precipitated. The author finds, however, that when 5 c.c. of a solution of mercuric sulphate, prepared from 5 grams of mercuric oxide, 20 c.c. of sulphuric acid, and 100 c.c. of water is added to 10 c.c. of urine, the mixture allowed to remain five minutes and then filtered, the filtrate gives the spectroscopic test.

E. W. W.

Organic Chemistry.

Action of Potassium Cyanide on Bromopicrin. By ROLAND SCHOLL and MORDKO BRENNEISEN (*Ber.*, 1898, 31, 642—653). When aqueous potassium cyanide is added to a well stirred alcoholic solution of bromopicrin, *symmetrical tetranitrodipotassioethane*,

$$C(NO_2)_2K\cdot C(NO_2)_2K,$$

is precipitated as a yellow, crystalline powder, which, when pure, forms dichroic yellow prisms and explodes at 270—275° or on percussion. When the aqueous solution is acidified with sulphuric acid, ether extracts from it an oil of characteristic odour, which, however, yields a white, and not a yellow, salt with potash. This substance is, therefore, not, as was expected, tetranitroethane; it is being more closely examined. The *silver* salt is a yellowish-red, crystalline precipitate. Tetranitropotassioethane is converted almost quantitatively, by the action of bromine, into *tribromotrinitroethane*, $C(NO_2)_2Br\cdot C(NO_2)Br_2$, which is a white, crystalline powder, and decomposes and melts when rapidly heated at 140°, when slowly heated, at 124—125°. It is decomposed when heated with water, a volatile oil and cyanogen bromide being formed, whereas it is not affected by boiling nitric acid. When it is distilled under a pressure of 50 mm., it yields three chief decomposition products, together with bromine and nitric oxide. The fraction of lowest boiling point consists of dibromodinitromethane, $C(NO_2)_2Br_2$, identical with that described by Losanitsch (Abstr., 1884, 277). The second fraction, boiling at 108—110° under a pressure of 19 mm., consists of *tribromonitroethylene*, $C(NO_2)Br\dot{:}CBr_2$, which is a heavy, yellow oil with a penetrating odour; it unites with bromine to form a white, crystalline substance melting at 147°, probably *pentabromonitroethane*, $C_2Br_5\cdot NO_2$. Finally, the residue left after the distillation of the tribromonitroethylene probably consists of *symmetrical dibromodinitroethylene*, $C(NO_2)Br\dot{:}C(NO_2)Br$, and crystallises in yellowish needles melting at 45°.

Tribromotrinitroethane is converted by aqueous potash into monobromodinitropotassiomethane, together with a small quantity of an oil smelling like bromopicrin, whilst potassium carbonate regenerates symmetrical tetranitropotassioethane.

These reactions show that tribromotrinitroethane has the constitution assigned to it above, from which that of the tetranitropotassioethane follows.
A. H.

An Impurity in Bromopicrin. By ROLAND SCHOLL and MORDKO BRENNEISEN (*Ber.*, 1898, 31, 654—655. Compare the foregoing abstract).—When bromopicrin is slowly dropped into a well cooled and thoroughly agitated solution of 50 per cent. aqueous potash, and then saturated with carbonic anhydride, a yellow salt crystallises out; after recrystallisation from water, this forms lustrous, yellow crystals which consist of bromodinitropotassiomethane, $C(NO_2)_2BrK$, exploding at

155°. It is probably formed by the action of a trace of calcium nitrite on bromopicrin during the distillation of picric acid with calcium hypobromite. A. H.

Direct Nitration of the Paraffins. By R. A. Worstall (*Amer. Chem. J.*, 1898, **20**, 202—217).—Konowaloff (Abstr., 1892, 575) has stated that, when normal hexane or octane is heated with nitric acid in sealed tubes at 130°, secondary nitro-compounds only are formed; the author finds, however, that primary compounds alone are produced by nitration in an open vessel.

When normal hexane is boiled with nitric acid (sp. gr. = 1·52 or 1·42), either alone or with concentrated sulphuric acid, during several days, a 60 per cent. yield of crude nitro-product is obtained; it consists of *primary nitrohexane*, $C_6H_{13}\cdot NO_2$, a light yellow oil which boils at 180—183°, is volatile with steam, and gives the nitrolic acid test; together with a *dinitrohexane*, probably primary, which has a light-yellow colour, is decomposed when distilled, and is sparingly soluble in aqueous alkalis, but readily in their alcoholic solutions, a red coloration being produced in both cases. On reducing nitrohexane, a primary *amine* is formed which gives the isonitrile and thiocarbimide reactions, and yields a *platinochloride*, $(C_6H_{13}\cdot NH_2)_2,H_2PtCl_6$.

Normal heptane is more easily nitrated than normal hexane, a primary *nitroheptane*, $C_7H_{15}\cdot NO_2$, being formed, which boils at 193—196°, gives the nitrolic acid test, and is easily reduced to a primary *amine*. *Primary dinitroheptane*, $CH_3\cdot[CH_2]_5\cdot CH(NO_2)_2$, is a clear yellow oil, which is formed, together with nitroheptane, when the nitration is carried out with a mixture of nitric and sulphuric acids; it decomposes on being distilled, gives a red coloration with alkalis, and on reduction gives rise to ammonia and hydroxylamine, with, possibly, some heptoic acid.

A primary nitro-octane, apparently identical with that prepared by Eichler (Abstr., 1880, 229) from octylic iodide, is formed on heating normal octane with nitric acid (sp. gr. = 1·42), or with this and concentrated sulphuric acid; it boils at 205—210°, gives the nitrolic acid test, and is easily reduced to a primary *octylamine*, which gives the isonitrile and thiocarbimide reactions, and yields a *platinochloride*, $(C_8H_{17}NH_2)_2,H_2PtCl_6$.

Fuming nitric acid (sp. gr. = 1·52) oxidises normal octane. *Primary dinitro-octane*, $CH_3\cdot[CH_2]_6\cdot CH(NO_2)_2$, is a clear yellow oil which closely resembles dinitrohexane and dinitroheptane; on reduction, it yields ammonia, hydroxylamine and octoic acid.

The products of oxidation by nitric acid of normal hexane, heptane, and octane, are invariably carbonic anhydride and acetic, succinic, and oxalic acids; the latter, however, is generally produced in very small quantity (0·04 per cent.), Schorlemmer stating that he was unable to detect its formation from hexane, octane, or diamyl. W. A. D.

Masut. By Nicolai Kromer (*Zeit. anal. Chem.*, 1898, **37**, 176—181).—The residue from the refining of Baku petroleum is much used in Russia as a fuel under the name of "masut"; the commercial article, however, frequently consists of imperfectly distilled crude oil, and numerous conflagrations have resulted from the

presence of hydrocarbons of low-boiling point. The examination of 100 samples showed that several of them had a flashing point as low as 47°, and one sample gave 82 per cent. of distillate below 310°.

The paper contains a tabular statement of all the results obtained.

M. J. S.

Synthesis and Constitution of Isoprene. By WILHELM EULER. (*J. pr. Chem.*, 1898, **57**, 131—159).—A more detailed description of work on isoprene already published (see Abstr., 1897, i, 585).

A. W. C.

Ferrocyanides of Zinc and Manganese. By GEORGE C. STONE and D. A. VAN INGEN (*J. Amer. Chem. Soc.*, 1897, **19**, 542—547. Compare Abstr., 1896, ii, 126 and 547).—Determinations of the ratio of iron to zinc in the precipitate formed on adding an excess of potassium ferrocyanide to a cold neutral solution of a zinc salt show that it has the composition $ZnK_2FeC_6N_6$; the precipitate obtained when the zinc is in excess has the same composition. Precipitation in cold solutions containing 5 per cent. by volume of hydrochloric acid gives a product $Zn_{10}K_8(FeC_6N_6)_7$; whilst from hot solutions, either acid or neutral, the compound $Zn_4K_4(FeC_6N_6)_3$ is obtained. The precipitate formed in solutions containing one-seventh per cent. by volume of hydrochloric acid had the composition $Zn_4K_4(FeC_6N_6)_3$, whilst a salt purchased as $Zn_2FeC_6N_6$ gave numbers corresponding to $Zn_3K_2(FeC_6N_6)_2$.

From cold neutral solutions of manganese, the salt $MnK_2FeC_6N_6$ is precipitated on adding potassium ferrocyanide, when either the latter or the manganese is in excess. Precipitation from a cold solution containing 5 per cent. by volume of hydrochloric acid gives rise to the salt $Mn_4K_4(FeC_6N_6)_3$; whilst from hot solutions, whether neutral or acid, the compound $MnK_2FeC_6N_6$ is precipitated. The same salt is obtained from a cold solution containing one-seventh per cent. by volume of hydrochloric acid.

In the volumetric method of estimating zinc by potassium ferrocyanide, using an uranium salt as indicator on a porcelain plate, the end point corresponds with a salt of the composition $Zn_2FeC_6N_6$ when the solution contains one-seventh per cent. by volume of hydrochloric acid; when, however, the solution is hot and contains 10 per cent. of acid, it corresponds with the salt $Zn_3K_2(FeC_6N_6)_2$. If the test be made on a filter-paper, so that the uranium does not come into contact with the precipitate, but only with the clear filtrate from it, the end point corresponds with the compound $Zn_4K_4(FeC_6N_6)_3$ when the solution is cold and contains one-seventh per cent. of hydrochloric acid; copper salts and ferric chloride, under identical conditions, indicate the same compound. A concentrated solution of cobalt when brought into contact, but not mixed with the zinc solution, also indicates $Zn_4K_4(FeC_6N_6)_3$, but very dilute cobalt solution, when mixed with the zinc solution, gives the reaction at a point corresponding with $Zn_3K_2(FeC_6N_6)_2$. With cold solutions of manganese containing one-seventh per cent. by volume of hydrochloric acid, strong cobalt and uranium solutions on filter-paper indicate the formation of the

salt $MnK_2FeC_6N_6$, whilst with very dilute cobalt solution the end point corresponds with the compound $Mn_3K_2(FeC_6N_6)_2$. The authors consider that cobalt is the most satisfactory indicator, since it develops a colour instantaneously, whilst the others do not. W. A. D.

Ferrocyanides of Zinc and Manganese. By EDMUND H. MILLER and JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1897, **19**, 547—558. Compare Abstr., 1897, ii, 433, and preceding abstract).—The ferrocyanides of zinc and manganese, after being dried at 100°, still retain a considerable proportion of water, although probably not as water of crystallisation, as Wyrouboff has stated (Abstr., 1877, ii, 19); it was determined by heating the salt in a current of dry air until it began to char, and absorbing the water formed, by calcium chloride. Zinc ferrocyanide precipitated from a cold, slightly acid solution of zinc chloride by potassium ferrocyanide, the zinc chloride being in excess, contains 9·37 per cent. H_2O, after being dried at 100°, whilst a determination of cyanogen, zinc, iron, and potassium in the completely dried salt, point to the composition of the latter being $Zn_3K_2(FeC_6N_6)_2$. The ratio of zinc to iron in the salt precipitated by an excess of potassium ferrocyanide agrees with the formula $Zn_7K_6(FeC_6N_6)_5$.

Manganese ferrocyanide precipitated from a cold, slightly acid solution of manganous chloride, the latter being in excess, contains 3 23 per cent. H_2O after being dried at 100°, and appears to have the composition $9MnK_2FeC_6N_6 + Mn_2FeC_6N_6$, rather than $5Mn_2FeC_6N_6 + 4K_4FeC_6N_6$ as given by Wyrouboff. An excess of potassium ferrocyanide precipitates a salt of different composition, the ratio of zinc to manganese being that required by the formula $15MnK_2FeC_6N_6 + Mn_2FeC_6N_6$.

Since the composition of the ferrocyanides obtained with an excess of a zinc or manganese salt is different from that formed by an excess of potassium ferrocyanide, an explanation is afforded of the fact that all attempts to estimate zinc or manganese by adding an excess of potassium ferrocyanide and titrating back with potassium permanganate have failed. W. A. D.

Inversion of Saccharose by Water. By BOHUSLAV RAÝMAN and OTTOKAR SULČ (*Chem. Centr.*, 1897, ii, 476; from *Rozpravy česke akad.* **5**, [Klasse 2], 33).—When a 20 per cent. aqueous solution of saccharose was boiled in a glass flask standing on gauze and fitted with a reflux condenser, the rotation sank from +11·66° to +5·94° (100 mm. tube); when heated on the water bath, it sank to +6·82°, and by heating in a platinum flask standing on asbestos, it was reduced from +13·25° to −3·42°. The amount of inversion is less when the solution is heated under pressure at 100° than when boiled under atmospheric pressure. Levulose is largely decomposed at 105°, and at 120° yields formic acid, furfuraldehyde, carbonic anhydride, pyrolevulinic acid, and humus-like substances. Dextrose is only slightly decomposed at 120°, a reducing substance of less optical activity being formed, but it is almost completely decomposed at 180°. Saccharose is only inverted to a very small extent by the action of amido-acids at 100°, but to a large extent

when heated at 105° under pressure. The greater the molecular weight of the acid employed, the less the amount of inversion effected.

E. W. W.

Gentianose. By ÉMILE BOURQUELOT and L. NARDIN (*Compt. rend.*, 1898, **126**, 280—281).—Fresh gentian roots are cut into thin slices and added gradually to alcohol of 95° previously heated to boiling, the boiling being continued in a reflux apparatus for 20 to 25 minutes; any ferment present in the root is thus destroyed. The liquid is filtered, distilled, the residue neutralised with calcium carbonate, again filtered, and finally evaporated to a very thick syrup. After remaining at the ordinary temperature for some weeks, the semi-crystalline mass is dissolved in the smallest possible quantity of hot water, and 4·5 parts of hot alcohol of 95° is added for every 1 part of water, after which the liquid is allowed to remain at the ordinary temperature for 15 hours; the clear solution is then decanted off into another vessel, in which it gradually crystallises. The compound is purified by recrystallisation from alcohol of 95°.

The gentianose thus obtained, forms anhydrous lamellæ which burn without residue, and are completely soluble in water, yielding colourless solutions. It melts at 207—209°, and is dextrogyrate; $[\alpha]_D = +31\cdot25°$, and no phenomenon of birotation could be recognised. Gentianose does not reduce cupric salts in presence of potassium hydroxide, but if boiled with dilute sulphuric acid, it becomes lævogyrate and acquires considerable reducing power. C. H. B.

Synthesis of Nitrogenous Compounds by means of Nitric Oxide. By WILHELM TRAUBE (*Annalen*, 1898, **300**, 81—128).—In several papers recently published, the author has shown that, under suitable conditions, nitric oxide unites with a large number of organic compounds. The power of combining with nitric oxide is exhibited by all those compounds which yield isonitroso-derivatives under the influence of nitrous acid, namely, ethylic acetoacetate, ethylic malonate, and its alkylic derivatives, ethylic acetylsuccinate, nitroparaffins, ketones having a methenyl, methylene, or methyl group adjacent to the carbonyl radicle, diketones, ethylic phenylacetate, benzylic cyanide, resorcinol, phloroglucinol, ethylic succinylsuccinate, menthone, carvone, and similar compounds. Combination of these substances with nitric oxide, however, occurs only in presence of alkalis.

The "nitric oxide reaction," as the author refers to this method of synthesis, involves the replacement of hydrogen by the group N_2O_2H. In order to distinguish the compounds obtained by this means from the nitramines of Franchimont, they are called isonitramines (compare Hantzsch, this vol., i, 247). They are identical with the products of the action of nitrous acid on substituted hydroxylamines, and are also obtained by the hydrolysis of von Baeyer's bisnitrosyl compounds with hydrochloric or sulphuric acid.

Nitroethylisonitramine, $NO_2\cdot CHMe\cdot N_2O_2H$, is obtained by the action of nitric oxide on the sodium derivative of nitro-ethane suspended in an alcoholic solution of sodium ethoxide (1 mol.). The *sodium* derivative is hygroscopic, but the solution yields crystalline derivatives with certain metallic salts; lead acetate gives a colourless precipitate, copper

sulphate a green, and silver nitrate a colourless derivative, which rapidly becomes black. The *barium* derivative separates in small, colourless plates, and is almost insoluble in water; it explodes when heated, and, like the other derivatives, is decomposed by mineral acids, yielding nitric oxide and ethylnitrolic acid.

The sodium derivative obtained by the action of nitric oxide on sodium nitromethane has not been obtained in the purified state; it is hygroscopic, and explodes with violence when heated.

Nitropropylisonitramine, $NO_2 \cdot CHEt \cdot N_2O_2H$, is prepared from nitropropane. The *sodium* derivative is not hygroscopic, and separates in slender needles on adding alcohol to the aqueous solution; it contains $\frac{1}{2}H_2O$, which cannot be removed without further decomposing the substance. Mineral acids eliminate nitric oxide, producing propylnitrolic acid. Metallic derivatives are precipitated from a solution of the sodium compound on adding metallic salts; all such derivatives explode with violence when heated.

Nitropentylisonitramine, $C_4H_9 \cdot CH(NO_2) \cdot N_2O_2H$, is obtained by the action of nitric oxide on nitropentane. The *sodium* derivative is hygroscopic, but the *barium* derivative is insoluble in water; the metallic derivatives explode less violently than those of the lower homologues.

Methylenedi-isonitramine, $CH_2(N_2O_2H)_2$, arises from acetone, mesitylic oxide, methyl isopropyl ketone, acetophenone, and ethylic dimethylacetate on application of the nitric oxide reaction; it is most conveniently prepared from acetone (Abstr., 1895, i, 124). The sodium derivative contains $1H_2O$, and crystallises in the rhombic system; $a:b:c = 0.5832:1:0.3536$. The *lead* derivative is anhydrous, and the *potassium* derivative which dissolves with some difficulty in water, is insoluble in absolute alcohol; the *ammonium* derivative melts at 157°, and the aniline derivative is crystalline. The *dimethylic ether* occurs in two forms, the α-modification, which crystallises from alcohol and melts at 134°, and the β-modification, which dissolves more freely in alcohol, crystallises from water in intensely yellow leaflets, and melts at 74°; the β-compound is decomposed by ammonia and alkalis, yielding nitrogen, nitrous oxide, and formaldehyde. The α-ether crystallises in the rhombic hemimorphic system; $a:b:c = 0.4550:1:1.0618$. The *diethylic ether* is also produced in two modifications. The α-ether crystallises from hot alcohol in colourless leaflets and melts at 82°; it is indifferent towards mineral acids, but yields ammonia and hydrazine under the influence of sodium amalgam. The β-ether is an oil, and when treated with mineral acids yields colourless gas and formaldehyde.

Ethylidenedi-isonitramine, $CHMe(N_2O_2H)_2$, is produced from diethyl ketone and from methyl ethyl ketone; the *lead* derivative is anhydrous, and crystallises in small cubes. The *dimethylic ether* melts at 75°, and crystallises in the rhombic system; $a:b:c = 0.4023:1:0.5641$. Free ethylidenedi-isonitramine is resolved by mineral acids into acetaldehyde and hydroxylamine, with elimination of oxides of nitrogen; sodium amalgam gives rise to hydrazine.

Propylidenedi-isonitramine, $CHEt(N_2O_2H)_2$, forms a *lead* derivative which is anhydrous. The *dimethylic ether* melts at 56°, and crystallises in the monoclinic system; $a:b:c = 0.3064:1:0.3845$. $\beta = 103° 5'$.

Benzylidenedi-isonitramine, $CHPh(N_2O_2H)_2$, is prepared from methyl benzyl ketone, and from ethylic phenylacetate; the *sodium* derivative is hygroscopic, and the *barium* derivative is a colourless, crystalline powder. The *dimethylic ether* melts at 152°, and crystallises in the rhombic system; $a:b:c = 0{\cdot}5413:1:1{\cdot}1762$. The *diethylic ether* melts at 133°.

Isonitraminobenzoylacetone, $COPh{\cdot}CHAc{\cdot}N_2O_2H$, is obtained by the action of nitric oxide on benzoylacetone. The *sodium* derivative contains $1H_2O$, and separates in the form of a white, crystalline powder on adding alcohol to the aqueous solution; it is not hygroscopic, and the aqueous solution gradually decomposes spontaneously, yielding gas.

Di-isonitraminobenzylic cyanide, $CN{\cdot}CPh(N_2O_2H)_2$, is prepared from benzylic cyanide; the *sodium* derivative is a white, crystalline powder, and is not hygroscopic. The *barium* derivative is anhydrous, and dissolves with great difficulty in water. M. O. F.

Reactions of Phospham. By RAYMOND VIDAL (*Chem. Centr.*, 1897, ii, 517; from *Mon. Scient.*, [iv], 11, ii, 571).—A 90 per cent. yield of phospham is obtained by heating ammonium chloride with phosphorus pentasulphide in theoretical proportions. When phospham is heated with an alkali carbonate, phosphate, R_2HPO_4, and cyanate are formed; by adding carbon, a cyanide is obtained; with iron, a ferrocyanide, and with sulphur, a thiocyanate. When heated with oxalates, phospham yields a phosphate and cyanogen; with methylic or ethylic alcohol, it reacts in accordance with the equations :—$PN_2H + 4ROH = OH{\cdot}PO(ONH_2R_2)_2$; $OH{\cdot}PO(ONH_2R_2)_2 = PO_3NH_3R + ROH + NHR_2$; with propylic alcohol, the action is complex, propylamine and propylic oxide being formed. Diphenylamine is obtained when phospham is heated with phenol, and on boiling ethylenic glycol with phospham, ammonium hydrogen phosphate and acetylene are formed.

E. W. W.

Hexalkyldiarsonium Compounds. By ALFRED PARTHEIL and E. AMORT (*Ber.*, 1898, 31, 596—598).—By heating mercury arsenide, As_2Hg_3 (this vol., ii, 334), with an alkylic iodide in a sealed tube at 180°, a hexalkyldiarsonium mercuriodide, $As_2R_6I_2 + 2HgI_2$, is obtained. Silver chloride converts this into a compound of the hexalkylarsonium iodide with mercuric chloride; silver hydroxide, into the hexalkyldiarsonium hydroxide, from which the salts can be prepared by neutralisation with acids. The hydroxides themselves cannot be isolated; the propyl compound is decomposed when distilled, even under diminished pressure, and propylcacodylic acid is found in the distillate. The substances prepared are enumerated below with their melting points.

Hexamethyldiarsonium compounds: *mercuriodide*, yellow, 184°; *iodide*, 171° with decomposition; *mercurochloride*, 211°; *platinochloride*, yellow, unmelted at 255°.

Hexethyldiarsonium compounds: *mercuriodide*, yellow, 112°; *iodide*, 162° with decomposition; *chloride*; *mercurochloride*, 137°; *platinochloride*, yellow, 237°.

Hexapropyldiarsonium compounds: *mercuriodide*, yellow, 120°; *iodide*, 150° with decomposition; compound of the latter with

mercuric chloride; *mercurochloride*, 169°; *platinochloride*, reddish-yellow, 189°.

Hexisopropyldiarsonium compounds: *mercuriodide*, yellowish-white, 114°; *iodide*, 150° with decomposition; *mercurochloride*, 171°; *platinochloride*, yellow, 211°.

Hexabutyldiarsonium compounds: *mercuriodide*, yellow, 109°; *iodide*, 145° with decomposition; *platinochloride*, yellow, 147°.

C. F. B.

Preparation of Acetone Oil and Methyl Ethyl Ketone from Suint. By A. Buisine and P. Buisine (*Compt. rend.*, 1898, **126**, 351—353.)—The fatty acids obtained from the water used for the desuintage of wool (this vol., i, 175) is neutralised with lime, evaporated to dryness, and the product distilled. It yields 45 to 50 per cent. of its weight of acetone oil of sp. gr. = 0·838, 80 per cent. of which is soluble in water. When fractionated, this oil yields 60 per cent. of methyl ethyl ketone, a compound hitherto difficult to obtain in any considerable quantity. This acetone oil is very suitable for the "denaturation" of alcohol, and since methyl ethyl ketone has almost the same boiling point as alcohol, the separation of the two is very difficult.

C. H. B.

Electrolysis of the Alkali Salts of Organic Acids. By Julius Petersen (*Chem. Centr.*, 1897, ii, 518—520; from *Bull. Acad. roy. Danemark*, 1897, 397—432).—From the results obtained by previous investigators, supplemented by his own work on the electrolysis of acid solutions of the potassium salts of acetic acid and its homologues, the author represents the decomposition as taking place in accordance with the following equations:—

(1) $2C_nH_{2n+1}\cdot CO_2H = 2C_nH_{2n+1}\cdot CO_2 + H_2$.

(2) $2C_nH_{2n+1}\cdot CO_2 + H_2O = 2C_nH_{2n+1}\cdot CO_2H + O$.

(3) $2C_nH_{2n+1}\cdot CO_2 = C_{2n}H_{4n+2} + 2CO_2$.

(4) $2C_nH_{2n+1}\cdot CO_2 = C_nH_{2n+1}\cdot CO_2\cdot C_nH_{2n+1} + CO_2$.

(5) $2C_nH_{2n+1}\cdot CO_2 + O = 2C_nH_{2n} + H_2O + 2CO_2$.

When a dilute acid solution of sodium formate is electrolysed, as the current intensity increases the amount of carbonic anhydride formed by oxidation of the acid decreases, but, in a concentrated solution, variation of current intensity has little effect on this action. As the concentration of the solution is diminished, more oxygen and less carbonic anhydride are liberated.

The end products of the electrolysis of these acids are those of (3), (4), and (5). Acetic acid is decomposed mainly in accordance with (3) and (1); in this case, the formation of methylic acetate was confirmed. Propionic, normal butyric, and isobutyric acids are decomposed for the most part according to (5), and (4) becomes more important as (3) diminishes. In the case of propionic acid, ethylic propionate was found amongst the products of electrolysis. The quantity of butane liberated varied directly, and the quantity of oxygen inversely, with the current intensity and the concentration of the solution. A solution containing 14 per cent. of the salt gave the maximum yield

of ethylene. Butyric acid yields propylic and isopropylic butyrates. More hexane and propylene and less hydrogen are liberated when the current intensity or the concentration of the solution is increased. Isobutyric acid yields di-isopropyl and isopropylic butyrate. Variations of current intensity or concentration of the solution have the same effect as in the preceding case, but the amount of di-isopropyl formed is less than the amount of hexane obtained from the normal acid under like conditions.

When oxalic acid is electrolysed, the current intensity has no effect on the nature of the products, but as the solution is diluted the amount of oxygen liberated increases. Malonic acid yields a small quantity of ethylene; the amount of carbonic oxide increases slightly with current intensity but much more with the concentration of the solution. An acid solution of potassium succinate gives neither carbonic oxide nor acetylene. The amount of ethylene liberated, however, increases with the current intensity and the concentration of the solution much more than in the case of any other acid; a 0·5 per cent. solution of the salt with 1·5 ampères at 0° gave 0·25 per cent. of ethylene in the gas obtained, and a 40 per cent. solution, 23·7 per cent. of this gas. Isosuccinic acid yields, not only oxygen, hydrogen, carbonic anhydride, and carbonic oxide, but also traces of ethylene and acetaldehyde. Less oxygen is liberated than in the case of succinic acid, some of the oxygen being used for the formation of acetaldehyde. The amount of ethylene and of acetaldehyde both vary directly with the current intensity and the concentration of the solution. Phenylacetic acid yields small quantities of benzaldehyde and benzoylphenylic acetate in addition to oxygen, hydrogen, and carbonic anhydride.

E. W. W.

Condensation Products of Aldehydes. Part III. Octoglycol Isobutyrate from Isobutaldehyde. By MAXIMILIAN BRAUCHBAR and LEOPOLD KOHN (*Monatsh.*, 1898, **19**, 16—55. Compare Fossek, Abstr., 1884, 37).—When isobutaldehyde is heated with sodium acetate in sealed tubes, *octoglycol isobutyrate* is obtained boiling at 138° under a pressure of 18 mm., or 250—252° at atmospheric pressure. The first step in the reaction is the production of an intermediate aldol condensation product, $OH\cdot CHPr^{\beta}\cdot COPr^{\beta}$, which then combines with a third molecule of the aldehyde in the following manner, $OH\cdot CHPr^{\beta}\cdot COPr^{\beta} + CHPr^{\beta}O = OH\cdot CHPr^{\beta}\cdot CMe_2\cdot CH_2\cdot O\cdot COPr^{\beta}$.

Octoglycol isobutyrate is a colourless oil of pleasant odour and bitter acrid taste; it does not soldify on cooling, has a sp. gr. = 0·9438 at 15·7°/15·7° and molecular weight agreeing with the formula $(C_4H_8O)_3$, and not with $(C_4H_8O)_2$, as stated by Fossek. When treated with alcoholic potash, it is decomposed into octoglycol and isobutyric acid. It does not react with hydroxylamine, cannot be reduced, and is not altered on heating at 260° for 6 hours, which facts prove the non-existence of a carbonyl group in the substance.

On acetylation, it yields a *monacetyl* derivative differing but slightly in odour from the original substance, and boiling at 136° under a pressure of 17 mm. When heated in sealed tubes with sulphuric acid, it is converted into isobutyric acid and the oxides of octoglycol.

When octoglycol isobutyrate is oxidised with potassium permanganate, there are obtained, besides isobutyric acid and an oxy-acid, $C_8H_{16}O_3$, (*a*) a thick, colourless oil boiling at 156—160° under a pressure of 17 mm., and still under investigation, (*b*) a colourless *oil*, $C_{12}H_{22}O_3$, boiling at 135° under a pressure of 17 mm., possessing a strong, although not unpleasant, odour; it contains no hydroxyl groups and on hydrolysis yields isobutyric acid and an oil smelling strongly of camphor; it is probably the isobutyrate of the ketone alcohol corresponding with octoglycol.

The authors have also prepared octoglycol isobutyrate by heating together pure octoglycol and isobutyric acid, and find that it has properties identical with the above. A. W. C.

Alkylation of Isonitramino-derivatives of Fatty Acids. By Wilhelm Traube and Hans Sielaff (*Annalen*, 1898, **300**, 129—133).—The *methylic ether* of methylic isonitraminoacetate, $COOMe\cdot CH_2\cdot N_2O_2Me$, prepared by the action of methylic iodide on silver isonitraminoacetate, crystallises from alcohol in slender needles, and melts at 35°. The *amide* melts at 142°. Dilute hydrochloric acid resolves the ether into the *methylic ether* of isonitraminoacetic acid, $COOH\cdot CH_2\cdot N_2O_2Me$; the *potassium* salt crystallises in lustrous leaflets, and explodes violently when heated.

The *ethylic ether* of isonitraminoacetic acid is crystalline, and the *benzylic ether* melts at 135°.

The methylic ether of isonitraminopropionic acid yields the *amide*, $COONH_2\cdot CHMe\cdot N_2O_2Me$, which melts at 150°; the corresponding *amide* derived from isonitraminobutyric acid melts at 126°. The *dimethylic ether* of isonitraminobenzylacetic acid,

$$COOMe\cdot CH(CH_2Ph)\cdot N_2O_2Me,$$

melts at 82°. M. O. F.

Isonitraminoisobutyric Acid and Nitrosobutyric Acid. By Moses Gomberg (*Annalen*, 1898, **300**, 59—81. Compare Thiele and Heuser, Abstr., 1896, i, 340).—*Dinitrosohydrazoisobutyric acid*, $N_2(NO)_2(CMe_2\cdot COOH)_2$, produced by the action of nitrous acid on hydrazidoisobutyric acid, is a bright yellow, crystalline powder, which is very explosive in the dry state; it is fairly stable in presence of mineral acids, but is very sensitive towards alkalis, which liberate nitrogen from the substance. The nitrosamine explodes violently at 47—48°.

Isonitraminoisobutyric acid, $COOH\cdot CMe_2\cdot N(NO)\cdot OH$, is obtained by decomposing the nitrosamine with sodium phosphate or sodium borate, which eliminate nitrogen, adding a smaller quantity of hydrochloric acid than corresponds with the sodium present, and then extracting with ether; it separates from a mixture of ether and petroleum in large, transparent crystals, and melts at 94—95°. Hydroxyisobutyric acid is also produced in the change, and when alkalis are employed, is accompanied by the *compound*, $C_8H_{16}N_2O_7$, which crystallises from a mixture of ether and petroleum in long, white needles, and melts at 92—93°. Isonitraminoisobutyric acid crystallises in the rhombic system; $a:b:c = 0{\cdot}61160:1:0{\cdot}66712$. The *lead* salt crystallises in small, transparent prisms, and contains $1H_2O$; it undergoes no loss of

weight at 130°, and explodes at 160°. The *potassium* and *ammonium* salts are crystalline, and the *silver* salt is amorphous, becoming crystalline in the dark; from warm solutions, the silver salt separates in crystals.

Hydroxylaminoisobutyric acid, $COOH\cdot CMe_2\cdot NH\cdot OH$, is produced by the action of hydrochloric acid on isonitraminoisobutyric acid. It crystallises from hot water in two forms, large, regular rhombohedra, melting and decomposing at 195—196°, and long white prisms, which do not melt at 260°; recrystallisation from water frequently converts the former into the latter modification (compare Münch, Abstr., 1896, i, 203). The substance reduces neutral and ammoniacal solutions of silver nitrate, and also Fehling's solution, in the cold; nitrous acid regenerates isonitraminoisobutyric acid.

Methylic nitrosoisobutyrate, $COOMe\cdot CMe_2\cdot NO$, is obtained by the action of nitrous acid on methylic hydrazidoisobutyrate; it is a yellow oil which becomes emerald green when warmed, this colour disappearing as the liquid cools. It decomposes at 80—90°, and gives Liebermann's reaction; it reduces permanganate, but is indifferent towards ammoniacal silver and Fehling's solutions. A *polymeride* is formed along with the salt, and crystallises from a mixture of ether and petroleum; it melts at 105°. *Ethylic nitrosoisobutyrate* resembles the methylic salt. M. O. F.

The Tautomeric Forms of Ethylic Acetoacetate and similar Compounds. By ROBERT SCHIFF (*Ber.*, 1898, 31, 601—609. Compare this vol., i, 237).—The enolic form of the compound of ethylic acetoacetate with benzylideneaniline is converted into the ketonic form by the action of a trace of piperidine, whilst the inverse change is brought about by traces of sodium ethoxide.

The ethylic acetoacetate of commerce varies in constitution according to the care which has been exercised in its preparation. Since it is made in presence of sodium ethoxide, the pure product should be the enolic form, and this was found to be the case in one sample (prepared by Kahlbaum), whilst all the other samples consisted of a mixture of the ketonic and enolic forms.

It has been hitherto found impossible to isolate the ketonic form of free ethylic acetoacetate, since the product, obtained by treating the enolic form with piperidine and distilling, is a mixture of both varieties. The coloration with ferric chloride is conditioned by the presence of the hydroxyl group, but the intensity of the coloration depends, not only on the proportion of the enolic form which is present, but also on the nature of the solvent, and especially on the presence of moisture, in the absence of which only a very slight coloration is produced.

The isomeric benzylideneaniline compounds of ethylic acetoacetate are all decomposed by a trace of sodium methoxide in presence of alcohol in a similar manner. The enolic form yields aniline and the enolic form of *ethylic phenylcarbinol-acetoacetate*,

$$OH\cdot CMe\colon C(CHPh\cdot OH)\cdot COOEt,$$

which crystallises in white, silky needles, melts at 149·5—150°, and

gives a reddish-violet coloration with ferric chloride. The keto-compound, when treated in the same way, yields an isomeric *product*, CMeO·CH(CHPh·OH)·COOEt, melting at 133—134°. Finally, a mixture of the two forms yields a product which melts at 120°. If during this reaction, the solution is warmed, or allowed to remain too long in contact with sodium methoxide, only the enolic form of highest melting point is produced. When warmed with acetic anhydride, all three isomerides yield the same *acetyl* derivative, which is probably the enolic form, OH·CMe:C(CHPh·OAc)·COOEt, and melts at 150—151°. The isomerism of these compounds is due to the position of the mobile hydrogen atom of the acetoacetic group, and not in any way to the presence of an asymmetric carbon atom in the benzylideneaniline residue, for a substance like the benzylideneaniline compound of ethylic malonate, $NHPh·CHPh·CH(COOEt)_2$, can only be obtained in a single form.

Ethylic benzoylacetate combines with benzylideneaniline to form an additive *compound*, which separates in yellowish-white crystals melting at 101°; these constitute the ketonic form, and give no coloration with ferric chloride. If sodium ethoxide is added to the mixture of ethylic benzoylacetate and benzylideneaniline, the isomeric *enolic form* is obtained, which melts at 122° and gives a deep red colour with ferric chloride. Ethylic benzylidenediacetoacetate, prepared in the presence of piperidine, gives no coloration with ferric chloride and is the ketonic form; the enolic form is obtained by dissolving in alcoholic sodium ethoxide and precipitating with hydrochloric acid in the cold, but cannot be dried without passing back into the original ketonic form. In alcohol solution, it gives a deep greenish-violet coloration with ferric chloride. A. H.

New Compounds of the Cerite Metals. By André Job (*Compt. rend.*, 1898, **126**, 246—248).—When lanthanum oxalate is dissolved in hot, concentrated hydrochloric acid and the solution is allowed to cool, *lanthanum oxalochloride*, $La_2Cl_2(C_2O_4)_2 + 5H_2O$, separates in crystals which remain unaltered at 120°, but lose their water at 230°. When treated with boiling water, they are decomposed with formation of a soluble chloride and an insoluble oxalate. When the anhydrous salt is heated at a red heat, it loses no chlorine, but the residue has the composition of the oxychloride, $La_2O_2Cl_2$.

Cerium and didymium form analogous compounds, and oxalobromides and oxaloiodides can also be prepared. Oxalonitrates have been described by other observers.

The formation of these complex oxalates, and the retention of halogens in the residues obtained by heating them, may possibly explain the differences between the atomic weights as determined by different observers. C. H. B.

Dibromosuccinic Acids. By Wilhelm C. Lossen (*Annalen*, 1898, **300**, 1—5. Compare Abstr., 1897, i, 16).—A solution of dibromosuccinic acid which has been neutralised with soda, potash, baryta, or lime, decomposes on boiling in accordance with the three equations already put forward (*loc. cit.*), no material influence on the course of

the change being directly attributable to the nature of the base; the volume of water, however, with which the salts are boiled has a controlling influence on the progress of the decomposition.

It has been stated by Kekulé that a fourth equation must be recognised, namely, $C_4H_4Br_2O_4 + H_2O = HBr + C_4H_5BrO_5$, but the author has not succeeded in confirming this observation, having been unable to establish the existence of bromomalic acid. Kekulé's statement that the calcium tartrate, obtained from dibromosuccinates which have been boiled with water, contains $3H_2O$ is erroneous; the product is invariably a mixture of mesotartaric and racemic acids. M. O. F.

Decomposition of Normal Dibromosuccinates with Water. By WILHELM C. LOSSEN and ERNST REISCH (*Annalen*, 1898, **300**, 5—31. Compare foregoing abstract).—The authors have made a large number of observations regarding the behaviour of dibromosuccinates towards boiling water, which decomposes them according to the following equations.

$$\text{I.}\quad C_4H_2Br_2O_4X_2 = XBr + C_4H_2BrO_4X.$$
$$\text{II.}\quad C_4H_2Br_2O_4X_2 + H_2O = 2XBr + 2CO_2 + C_2H_4O.$$
$$\text{III.}\quad C_4H_2Br_2O_4X_2 + 2H_2O = 2XBr + C_4H_6O_6.$$

The following is a summary of the results.

1. The nature of the base employed has no influence on the course of the decomposition; this conclusion is opposed to that of Kekulé, who stated that baryta favours the production of bromomaleic acid, whilst tartaric acid is the main product when lime is employed. 2. Under parallel conditions, isodibromosuccinic acid decomposes more rapidly than dibromosuccinic acid. 3. Less bromine is eliminated from dibromosuccinic than from isodibromosuccinic acid. 4. The change represented by equation II is undergone by isodibromosuccinic acid to a greater extent than by dibromosuccinic acid. 5. Using 100 parts of boiling water, tartaric acid is produced in greater quantity from dibromosuccinic than from isodibromosuccinic acid; both acids yield approximately the same amount when the dilution is one-fifth as great, the quantity of tartaric acid arising from isodibromosuccinic acid being the same in both cases. 6. A preponderating amount of mesotartaric acid is obtained on boiling neutral dibromosuccinates with water, isodibromosuccinates yielding chiefly racemic acid. The change represented by equation II is favoured by the employment of 100 parts of boiling water, decomposition proceeding more in accordance with equation I when the dilution is one-fifth as great. Dibromosuccinates decompose more slowly than the isomerides. 8. Cold water also decomposes dibromosuccinic acid and its salts less rapidly than isodibromosuccinic acid and its salts. 9. The greater the degree of dilution, the slower is the elimination of bromine from dibromosuccinates. On the other hand, isodibromosuccinates lose bromine more rapidly in dilute than in concentrated solutions. 10. Calcium acetate accelerates elimination of bromine from the calcium salts. 11. Using 200 parts of water, bromine is removed more rapidly from dibromosuccinic acid than from sodium dibromosuccinate. 12. The converse is observed in the case of isodibromosuccinic acid and its sodium salt.

The behaviour of dibromosuccinic and isodibromosuccinic acids towards

water is not in agreement with the view expressed by J. Wislicenus, that the former corresponds to racemic, and the latter to mesotartaric acid. M. O. F.

So-called Bromomalic Acid. By WILHELM C. LOSSEN and ERICH MENDTHAL (*Annalen*, 1898, **300**, 31—39).—The authors cast doubt on the existence of bromomalic acid, which was claimed by Kekulé on the following grounds. (1) When sodium dibromosuccinate is boiled with water, hydrogen sodium bromomalate is produced, which, when dried at 100°, has the formula $C_4H_4BrO_5Na$. (2) Hydrogen sodium bromomalate yields calcium tartrate when boiled with lime-water; bromomaleic acid does not behave in this way. (3) The sodium salt is converted into a lead salt which has the composition of lead bromomalate, and has properties different from those of lead bromomaleate.

The authors give in detail their reasons for believing that the existence of bromomalic acid has yet to be proved. M. O. F.

Hydrogen Sodium Bromomaleate from Dibromosuccinic Acid. By WILHELM C. LOSSEN and WALTHER RIEBENSAHM (*Annalen*, 1898, **300**, 40—42. Compare foregoing abstract).—Under conditions apparently similar, hydrogen sodium bromomaleate separates from water in two forms, one containing $1H_2O$, the other being anhydrous. The authors have never obtained a salt which, after being dried at 100°, has the composition of hydrogen sodium bromomalate.

M. O. F.

Constitution of Ethylic Oxalolevulinate (Ethylic Diketopimelate). By WILHELM WISLICENUS, KARL GOLDSTEIN, and MAX MÜNZESHEIMER (*Ber.*, 1898, **31**, 622—626).—When ethylic oxalolevulinate is treated with aluminium amalgam and water, it is converted into *ethylic hydroxyketopimelate*, $C_{11}H_{18}O_6$, which is a yellowish oil boiling at 210° under a pressure of 16 mm. This substance is reduced by hydriodic acid at 200° to normal pimelic acid, the formation of which proves the presence of a normal chain of 7 carbon atoms in oxalolevulinic acid, which therefore has the constitution

$$COOEt\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot COOEt.$$

The other reactions of oxalolevulinic acid and its ethylic salt all agree with this constitution. When the ethylic salt is distilled at the ordinary pressure, carbonic oxide is evolved and a distillate produced which boils at 105° under a pressure of 14 mm., but the reaction is by no means quantitative, and the product has not yet been obtained pure. It reacts with phenylhydrazine to form an unstable *compound*, which crystallises in plates and melts at 112°.

The pyrazole derivative of ethylic oxalolevulinate, on hydrolysis, yields a dicarboxylic acid melting at 165—167°, which loses carbon dioxide at 200° and is converted into 1-*phenylpyrazolepropionic acid*; this crystallises in long, colourless needles, melts at 120°, and boils at 235° under a pressure of 20 mm. The *silver* salt is a white, crystalline precipitate.

When ethylic oxalolevulinate is heated with 20 per cent. sulphuric acid, the *free acid* is obtained, but is very difficult to purify; it melts at 100—125° without decomposing, but when distilled decomposes into carbonic anhydride, carbonic oxide and levulinic acid. The acid

yields oxalic acid when heated with aqueous potash, and gives a red coloration with alcoholic ferric chloride. A. H.

Acetonedipyruvic Acid (Carbonyldimethylacrylic Acid). By OSCAR G. DOEBNER (*Ber.*, 1898, 31, 681—686.)—Pyruvic acid (90 grams) and acetone (45 grams) are dissolved in glacial acetic acid (120 grams), concentrated sulphuric acid (180 grams) is added, and the mixture heated at 105—110° for half an hour or until a portion poured into ice-cold water, and extracted with ether gives a crystalline product; the mass is then poured on to about 10 times its weight of ice and extracted with ether. A considerable quantity of *acetonedipyruvic anhydride*, $CO<\begin{matrix}CH\colon CMe\cdot CO\\CH\colon CMe\cdot CO\end{matrix}>O$ or $\begin{matrix}CMe\colon CH\\|\qquad\\CO—O\end{matrix}>C<\begin{matrix}CH\colon CMe\\\qquad|\\O—CO\end{matrix}$, separates out, and a further quantity may be obtained from the ethereal solution; after several recrystallisations from alcohol, it is obtained in the form of square plates melting at 166° and distilling at 234° under a pressure of 20 mm. The yield is 7 to 8 grams. It is readily soluble in hot methylic or ethylic alcohol and in benzene, also in cold acetic acid, chloroform, or methylal, but insoluble in water or carbon bisulphide; it reduces both ammoniacal silver nitrate and alkaline copper solutions.

The *sodium* salt, $C_9H_8O_5Na_2 + 6H_2O$, is obtained when an alcoholic solution of the anhydride is mixed with the requisite quantity of sodium hydroxide solution and then evaporated until the salt begins to crystallise; the anhydrous salt is deliquescent. The *potassium* salt, $C_9H_8O_5K_2 + 2H_2O$, loses its water at 130°, and is not so deliquescent in the anhydrous form as the sodium salt. The *silver*, *copper*, and *ethylic* salts have been prepared; the last named is an oil.

When an aqueous solution of the potassium salt (1 mol.) and of phenylhydrazine hydrochloride (2 mols.) is allowed to remain for 12 hours at the ordinary temperature, the *phenylhydrazide*,

$$CO(CH\colon CMe\cdot CO\cdot NH\cdot NHPh)_2,$$

of the acid separates as an oil; it crystallises from hot alcohol in well-developed, orange-red prisms melting at 206°. The potassium salt of the acid, when warmed with hydroxylamine hydrochloride, yields large colourless crystals of the *compound* $C_8H_{14}N_2O_4$ melting and decomposing at 209°; it has both acidic and basic properties, and is probably the oxime of N-hydroxydimethylpiperidonecarboxylic acid,

$$HO\cdot N\colon C<\begin{matrix}CH_2\cdot CMe(COOH)\\CH_2———CHMe\end{matrix}>N\cdot OH.$$

When the anhydride is heated with an excess of aqueous ammonia for 5 hours at 150°, a *diimide*, $C_9H_{10}N_2O_2$, is obtained in the form of colourless, crystalline needles subliming at about 280° and decomposing above 300°; it dissolves in warm acids and is decomposed on heating with alkalis.

When the anhydride is reduced with sodium amalgam and alcohol, *acetonedipropionic anhydride* is obtained in the form of an oil.

The anhydride (2 grams) when heated in chloroform (24 grams) solution with bromine (5 grams) for 5 hours at 110° yields a *tetrabromide*, which, after recrystallisation from alcohol, melts at 178°.

J. J. S.

Formamide and its Sodium and Silver Salts. By PAUL C. FREER and P. L. SHERMAN, junr. (*Amer. Chem. J.*, 1898, **20**, 223—228).—Formamide prepared by distilling ammonium formate under ordinary pressure is always contaminated with ammonium cyanide, formic acid, and ammonium formate; by heating ammonium formate, however, for 2 hours at 180° in an atmosphere of ammonia, and subsequently fractionating in the same atmosphere under ½ mm. pressure, pure formamide can be prepared. It solidifies at $-1°$ to a crystalline mass of needles, and has a sp. gr. = 1·16 at 4°; when heated above 100°, it is partially decomposed, the distillate between 203—216° containing water and ammonium cyanide.

Pure sodium formamide is quite stable at ordinary temperatures, but is rapidly decomposed by heat or moisture. *Silver formamide* is very sensitive to both light and heat.

The coloured silver compounds obtained by Titherley (Trans., 1897, 460) from the sodium derivatives formed by the action of acid amides on sodamide, probably owed their colour to his sodium derivatives being contaminated by free sodamide; the authors have prepared colourless silver derivatives by the same method. The arguments of Titherley as to their structure are therefore valueless. W. A. D.

Conversion of Methylpyromucic Acid into Aldehydopyromucic and Dehydromucic Acids. By HENRY B. HILL and HARRIS E. SAWYER (*Amer. Chem. J.*, 1898, **20**, 169—178).—On heating ω-bromomethylpyromucic acid (Hill and Jennings, Abstr., 1893, i, 311), dissolved in chloroform, with an excess of bromine, *ω-dibromomethylpyromucic acid* is formed, but only in very small quantity; it crystallises from benzene in small, greenish-white prisms, melts at 153°, is easily soluble in ether and chloroform, but almost insoluble in light petroleum and carbon bisulphide, and is decomposed by alcohol or water, the solution obtained in the latter case showing aldehydic properties.

Methylpyromucic chloride, $C_6H_5O_2Cl$, prepared by the action of phosphorus pentachloride or trichloride on methylpyromucic acid, melts at 28° to a colourless liquid which boils at 93—94° under 18 mm. pressure, and at 202° under 756 mm. pressure. When heated with bromine (2½ mols.) in bright sunlight at 150°, it yields *ω-dibromomethylpyromucic bromide*, which crystallises from chloroform or benzene in elongated plates and melts at 102°; it is decomposed by boiling water into tetrabromomethane, and, in much larger quantity, *aldehydopyromucic acid*, $C_6H_4O_4$. The latter crystallises from hot water in irregular, curved plates which are anhydrous, and from cold water in long, slender needles, with $1H_2O$, which rapidly effloresce; it is easily soluble in alcohol, less readily in ether and chloroform, and very sparingly in benzene, light petroleum, or carbon bisulphide. When quickly heated, it melts at 201—202°, but when slowly heated it sublimes and decomposes, the residue melting above 202°. The *oxime*, $C_6H_5NO_4$, crystallises from boiling water, and, when rapidly heated, melts and decomposes at 224—226°. The *phenylhydrazone*, $C_{12}H_{10}N_2O_3$, melts and decomposes at 176°, and is easily soluble in alcohol, less easily in ether, and almost insoluble in benzene, chloroform, and carbon bisulphide.

Dehydromucic acid, identical with that obtained from mucic acid, is

formed on oxidising a solution of aldehydopyromucic acid in dilute caustic soda with silver oxide; it was characterised by its barium salt.

W. A. D.

Condensation of Nitromethane with Substituted Aromatic Aldehydes. By THEODOR POSNER (*Ber.*, 1898, 31, 656—660).—ω-Orthodinitrostyrene, $NO_2\cdot C_6H_4\cdot CH:CH\cdot NO_2$, is formed when orthonitrobenzaldehyde is heated with nitromethane and zinc chloride at 160°, and is identical with the compound obtained by Priebs (Abstr., 1885, 161) by the nitration of ω-nitrostyrene. It was found impossible to obtain any definite product by the reduction of this substance. Orthonitrobenzylic chloride is converted by nitromethane and sodium ethoxide into *di-orthonitrobenzylnitromethane*,

$$NO_2\cdot CH(CH_2\cdot C_6H_4\cdot NO_2)_2,$$

which forms dark yellow crystals melting at 140—141·5°. The monosubstituted benzylnitromethane could not be obtained. Metanitrobenzaldehyde also reacts with nitromethane in the presence of zinc chloride to form ω-metadinitrostyrene, identical with the product obtained by Friedländer and Lazarus from metanitrocinnamic acid and nitric acid (Abstr., 1885, 1138), but no analogous compound could be obtained from any other aromatic aldehyde. Under the same conditions, orthamidobenzaldehyde yields *anhydro-orthamidobenzaldehyde*, $C_6H_4<\genfrac{}{}{0pt}{}{N}{\overset{||}{CH}}$, which forms large, pale yellow crystals melting at 214°; this substance is not identical with the base to which Rudolph assigns the same constitution (Abstr., 1880, 469). With acetic anhydride, it yields an *acetyl* derivative, $C_6H_4<\genfrac{}{}{0pt}{}{N}{\overset{||}{CAc}}$, which is a white, microcrystalline powder melting at 210°. The molecular weight, as determined by the boiling point method in acetic acid, agrees with the above formula.

A. H.

Derivatives of Catechol. By JULIUS HESSE (*Ber.*, 1898, 31, 598—601).—Dichloracetal does not react with phenol, resorcinol, quinol, hydroxyquinol, or pyrogallol, but it does react with catechol when it is heated with the disodium derivative of that substance for 16 hours at about 200°. The product, 1 : 2-*phenylenediethylglyoxal*, $C_6H_4:O_2:CH\cdot CH(OEt)_2$, is a thick liquid which boils at 150° (uncorr.) under 22 mm. pressure, decomposes when distilled under atmospheric pressure, and has a sp. gr. = 1·1252 at 14°; it forms a yellow *nitro*-derivative which melts and decomposes at 125°. When it is boiled for several hours with dilute sulphuric acid, and the alcohol and unchanged acetal are then distilled over with steam, 1 : 2′ : 6′-*trihydroxyhydrocumarone*, $OH\cdot C_6H_3<\genfrac{}{}{0pt}{}{\text{——O——}}{CH(OH)}>CH(OH)$, crystallises out from the residual liquid, as the latter cools, in yellowish, monoclinic crystals [$a : b : c = 2·218 : 1 : 3·564$; $\beta = 120° 14'$] which melt at 131°.

C. F. B.

3 : 4 : 5-Tribromaniline and Derivatives of Unsymmetrical Tribromobenzene. By C. LORING JACKSON and FRANK B. GALLIVAN (*Amer. Chem. J.*, 1898, 20, 179—189).—3 : 4 : 5-Tribromaniline, formed

on reducing the tribromonitrobenzene prepared by the diazo-reaction from dibromoparanitraniline, crystallises from dilute alcohol in slender, white needles and melts at 118—119°, whereas Körner (*Gazzetta*, 1874, 409) states that it decomposes above 130° without melting; it is converted by elimination of the amido-group into 1 : 2 : 3-tribromobenzene, and by the action of bromine into pentabromaniline. The *hydrochloride* crystallises from very dilute hydrochloric acid in white needles, but is partially decomposed on being boiled with water, although it is much more stable than 2 : 4 : 6-tribromaniline hydrochloride; the *hydrobromide* closely resembles the hydrochloride, whilst the *sulphate* crystallises from dilute sulphuric acid in white, lustrous plates. 3 : 4 : 5-*Tribromophenylurethane*, $C_6H_2Br_3\cdot NH\cdot COOEt$, formed on heating ethylic chlorocarbonate dissolved in benzene with 3 : 4 : 5-tribromaniline, crystallises from dilute alcohol in white, rhombic plates, melts at 169—170°, and is converted into diphenylcarbamide when heated with aniline.

3 : 4 : 5-*Tribromacetanilide* crystallises from alcohol in white, globular aggregates of needles, melts at 253—254°, is soluble in benzene but nearly insoluble in ether, chloroform, and light petroleum, and is not easily hydrolysed by sulphuric acid; it is converted by cold nitric acid (sp. gr. = 1·50) into 3 : 4 : 5-*tribromo-2-nitracetanilide*, which separates from alcohol and acetone in well-formed crystals, is almost insoluble in benzene, ether, and light petroleum, and is converted by boiling alkalis into 3 : 4 : 5-*tribromo-2-nitraniline*. The latter crystallises from alcohol in orange-yellow needles, is easily soluble in ether, benzene, and chloroform, and melts at 130°; on diazotising in alcohol acidified with sulphuric acid, and boiling, a *tribromonitrophenol* is formed which crystallises from alcohol and melts at 230°.

2 : 4 : 5-*Tribromophenylurethane* crystallises from dilute alcohol in long, slender needles, is easily soluble in benzene, chloroform, and glacial acetic acid, and melts at 101°; when heated with aniline, it yields diphenylcarbamide.

On adding 2 : 4 : 5-tribromacetanilide (Abstr., 1895, i, 212) to nitric acid (sp. gr. = 1·50), a 2 : 4 : 5-*tribromonitracetanilide* is formed, which crystallises from alcohol in small, pinkish-white needles, melts at 228°, and is easily soluble in the ordinary solvents; by boiling dilute sulphuric acid (sp. gr. = 1·44), it is converted into the corresponding 2 : 4 : 5-*tribromonitraniline*, which crystallises from alcohol in stout, yellow needles, melts at 130°, and is easily soluble in the ordinary solvents.

The authors find that the substance formed by the action of sodium ethoxide on 1 : 2 : 4-tribromo-3 : 5-dinitrobenzene is not a tribromodiethoxybenzene as formerly stated by them (Abstr., 1895, i, 212), but a *tribromonitrophenetoil*; at the same time, a bromodinitroresorcinol is formed, which yields an orange-yellow *barium* salt, $C_6HBr(NO_2)O_2Ba$, which is soluble in water and explodes when strongly heated.

W. A. D.

New Method for the Production of Acetyl Derivatives of Amido-compounds. By BRONISLAW PAWLEWSKI (*Ber.*, 1898, 31, 661—663).—The acetyl derivatives of aromatic amido-compounds can

be prepared by the aid of thiacetic acid much more readily than by the ordinary method with acetic acid, the reaction proceeding at a much lower temperature and much more rapidly, whilst the yield is almost theoretical. The reaction has been applied to the preparation of acetanilide, metanitracetanilide, which melts at 154—156°, acetomethylanilide, asymmetrical acetylphenylhydrazine, diacetylbenzidine and acetylanthranilic acid, and in all cases with good results.

A. H.

Action of Primary, Secondary, and Tertiary Bases on Orthoxylylenic Bromide. By ALFRED PARTHEIL and TH. SCHUMACHER (*Ber.*, 1898, **31**, 591—594).—The authors have been working on the same lines as Scholtz (this vol., i, 305), and have obtained substantially the same results, although frequently under somewhat different conditions, as, for instance, in alcoholic solution at 100°, instead of in chloroform solution at the ordinary temperature; the melting points observed differ slightly from those of Scholtz in many cases. The following compounds were not prepared by Scholtz; the numbers given are melting points.

2′-*Paraphenetidinedihydroisoindole*, $C_8NH_8\cdot C_6H_4\cdot OEt$, 204—205°. *Xylylenedipiperidyl picrate*, 227° with decomposition. *Xylylenedi-trimethylammonium bromide*, $C_6H_4(CH_2\cdot NMe_3Br)_2$, 207—208°; *platinochloride*, with $\frac{1}{2}H_2O$, orange-red, 253°, with decomposition; *aurochloride*, yellow, 249—250°; *mercurochloride*, 179—180°. With triethylamine in alcoholic solution, at 100°, xylylenic bromide yields *xylylenedi-triethylammonium bromide*, the *platinochloride* corresponding to which melts and decomposes at 237—238°; if the two substances are heated only until the bromide has just dissolved, the product is *xylylene-mono-triethylammonium bromide*, $CH_2Br\cdot C_6H_4\cdot CH_2\cdot NEt_3Br$, the *aurochloride* corresponding to which melts at 115—116°. C. F. B.

Hydramides and Isomeric Bases (Glyoxalidines). By MARCEL DELÉPINE (*Compt. rend.*, 1898, **126**, 343—346).

	Molecular heat of combustion.		Heat of formation
	Constant volume.	Constant pressure.	from elements.
Anisaldehyde, $C_8H_8O_2$	966·7 Cal.	967·3 Cal.	+63·1 Cal.
Anishydramide $(C_8H_8O)_3N_2$	3040·8	3042·8	+48·4
Anisine, $C_{24}H_{24}N_2O_3$	3024·6	3026·6	+64·6
Furfuramide, $C_{15}H_{12}N_2O_3$	1827·87	1828·15	+0·35
Furfurine, $C_{15}H_{12}N_2O_3$	1810·32	1810·6	+17·9

Furfurine hydrochloride, $C_{15}H_{12}N_2O_3$,HCl.—Heat of dissolution, −4·75 Cal. Heat of combination of solid furfurine with the dissolved acid, +6·55 Cal.; with the gaseous acid, +28·7 Cal.

It follows from the above results that the conversion of solid furfuramide into furfurine develops +17·55 Cal., and the conversion of anishydramide into anisine develops +16·2 Cal. Similar results have previously been obtained with hydrobenzamide and amarine. The thermal values explain why the isomerides of the hydramides cannot be reconverted into their generators by the action of acids, either strong or dilute. C. H. B.

Decomposition of Diazo-compounds: Reaction of Diazophenols and of the Salts of Chloro- and Bromo-diazobenzene with Ethylic and Methylic Alcohols. By FRANK K. CAMERON (*Amer. Chem. J.*, 1898, **20**, 229—251).—Paradiazophenol chloride yields phenol only when heated with ethylic or methylic alcohol, either alone or in presence of gaseous hydrogen chloride, ammonia, or sulphurous anhydride, no sulphonic acid being formed in the latter case; phenol is also formed on decomposing the diazo-salt with either of the above alcohols containing 20 per cent. of sulphuric acid or potassium hydroxide. A solution of paradiazophenol chloride in ether is not acted on by sulphurous anhydride.

Orthodiazophenol chloride similarly yields phenol only when treated with methylic or ethylic alcohol, either alone or in presence of gaseous hydrogen chloride or sulphurous anhydride.

Metadiazophenol chloride, when decomposed by dilute hydrochloric acid, yields resorcinol only, and phenol only when heated with ethylic or methylic alcohol.

Both the nitrates and sulphates of orthochlorodiazobenzene and orthobromodiazobenzene give the hydrogen reaction only when heated with either ethylic or methylic alcohol, chlorobenzene and bromobenzene being obtained respectively. The salts of metachlorodiazobenzene and of metabromodiazobenzene give the hydrogen reaction only when heated with ethylic alcohol; methylic alcohol, however, effects the introduction of a methoxy-group, metachloranisoil and metabromanisoil being respectively formed, together with, in smaller quantity, chlorobenzene and bromobenzene.

Parachlorodiazobenzene nitrate, on being heated with ethylic alcohol, gives rise principally to chlorobenzene, a small quantity of parachlorophenetoil and of 4 : 3-chloronitrophenol being also formed (compare Remsen and Orndorff, Abstr., 1888, 268; Beeson, Abstr., 1894, i, 329, and Chamberlain, Abstr., 1897, i, 562); parachlorodiazobenzene sulphate yields chlorobenzene only under similar conditions, whilst parabromodiazobenzene salts give rise to bromobenzene.

With methylic alcohol, parachlorodiazobenzene nitrate yields parachloranisoil and a small quantity of 1 : 3 : 4-chloronitrophenol, no chlorobenzene being formed; parabromodiazobenzene nitrate gives rise to parabromanisoil and 4 : 3-bromonitrophenol. The sulphates of parachlorodiazobenzene and parabromodiazobenzene produce respectively parachloranisoil and parabromanisoil only.

The following conclusions are drawn from this work and that of other authors. (1) That the alkyloxy-reaction is normal, whereas the hydrogen reaction is induced only by special conditions. (2) Regarding water as the first member of the series, the more complex the alcohol the greater is the tendency towards the hydrogen reaction. (3) The acid radicles, COOH, Cl, Br, NO_2, &c., especially when in the ortho-position, induce the hydrogen reaction (compare Remsen and Graham, Abstr., 1889, 975), their relative influence being probably according to the order in which they are named; when in the meta-position, their influence is not so great, whilst in the para-position it is still less.

W. A. D.

Diazo-cyanides and the Reaction of Diazo-compounds with Benzenesulphinic Acid. By ARTHUR HANTZSCH (*Ber.*, 1898, 31, 636—642).—Syndiazocyanides are formed when potassium cyanide is added to an acid solution of a diazonium salt, whereas, as a rule, diazoimidocyanides are produced when the diazonium salt is brought into an alkaline solution of potassium cyanide. In some cases, however, if only one product is stable, this is formed when either of these methods is employed. This is the case with pseudocumenediazocyanide melting at 38—39°, which can be preserved for some time at the winter temperature and has now been analysed. In other cases, the *syn*-diazocyanide is formed in the alkaline solution of potassium cyanide, and then, by contact with the solution, is converted into the diazoimidocyanide. Parabromodiazonium chloride acts in this way, the orange-red *syn*-diazocyanide being the first product, but changing in the course of 20 minutes into the brownish-yellow *parabrom*anti*diazoimidocyanide*, $C_6H_4Br\cdot N{:}N\cdot C(NH)\cdot CN$, which melts at 109—110°. Similar observations have been made on the behaviour of parachlorodiazonium chloride, the *diazoimido ether* of which melts at 103—105°. The *syn*-diazocyanides are also readily formed by the action of hydrocyanic acid on the diazo-oxides. Hydrochloric acid, on the other hand, reacts very slowly with these oxides and produces diazonium salts. The diazo-oxides react with potassium sulphite to form diazosulphonates, and with bezenesulphinic acid to produce diazosulphones. Thus parachlorodiazo-oxide is converted by hydrogen cyanide into parachloro*syn*diazocyanide, by potassium sulphite into parachloro-*syn*-diazosulphonate, and by benzenesulphinic acid into parachlorodiazophenylsulphone, which melts at 106—107°, and not at 102—103° as stated by Singer.

Most of the *syn*-diazocyanides combine with benzenesulphinic acid to form colourless additive compounds, from which the *anti*-cyanide is produced by removal of the acid. Pseudocumene*syn*diazocyanide, on the other hand, yields *pseudocumene*anti*diazosulphone*,

$$C_6H_2Me_2\cdot N{:}N\cdot SO_2Ph,$$

melting at 84°. The *anti*-diazosulphones do not form colouring matters with free naphthol, but do so in presence of an alkali. Benzenesulphinic acid yields colourless additive products with azobenzene and most of the aromatic diazo-compounds of the azo-type, but does not react with azo-compounds of the fatty series. When a solution of diazonium hydroxide is neutralised with benzenesulphinic acid, the solution contains diazonium benzenesulphinate, which is isomeric with benzenediazosulphone. This solution behaves in all respects as one of a diazonium salt, and gradually yields nitrogen and phenol, free benzenesulphinic acid being left in solution.

Benzenesulphinic acid reacts in a remarkable manner with diazoamido-compounds, forming a diazosulphone, which unites with 1 mol. of the acid, and a salt of the amine which contains the more negative radicle. Diazoamidobenzene yields aniline benzenesulphinate and the additive compound of benzenediazosulphone and benzenesulphinic acid melting at 175—176°. Parabromodiazoamidobenzene yields the *benzenesulphinate of parabromaniline*, and benzenediazosulphone; paranitrodiazoamidobenzene similarly yields *paranitraniline benzenesul-*

phinate, melting at 145—148°, and benzenediazosulphone. Paratoluenediazoamidobenzene, on the other hand, gives a mixture of the benzenesulphinates of aniline and paratoluidine, so that where the two groups are not very distinct in electrochemical character, the compound appears to act as a tautomeric one. A. H.

Ethylic Benzeneazocyanacetate. By HANS WEISSBACH (*J. pr. chem.*, 1898, **57**, 206—207).—When carbonic anhydride is passed into a dilute alcoholic solution of the potassium derivative of ethylic benzeneazocyanacetate at ordinary temperatures, the β-modification, doubtless really a phenylhydrazone, $N_2HPh\!:\!C(CN)\cdot COOEt$, is obtained, whereas if the temperature is increased to 60°, a third (γ) isomeric substance is also formed, separating from light petroleum in well-formed, red crystals melting at 84°; if kept in a state of fusion for some time, it is converted into a substance melting at 118°, possibly yet a fourth isomeride. The chemical behaviour and red colour of the γ-modification point to its being an azo-compound, namely, the true *ethylic benzeneazocyanacetate*, $CN\cdot CH(N_2Ph)\cdot COOEt$. It is not acted on by acetic chloride, whereas the corresponding α- and β-modifications are converted into a mixture of two isomeric *acetyl* derivatives, the one melting at 158° and the other at 166°. On hydrolysing with cold sodium hydroxide, both are converted into the same *acid*, $NPhAc\cdot N\!:\!C(CN)\cdot COOH$, forming small needles melting at 210°, and yielding an amide separating in yellow crystals. Further research on this subject is in progress. A. W. C.

Parahydroxyphenylhydrazine. By JULIUS ALTSCHUL (*J. pr. chem.*, 1898, **57**, 201—204).—Philipp (Abstr., 1893, i, 78) was unable to prepare parahydroxyphenylhydrazine by the V. Meyer-Lecco method, but the author finds that, by the action of alcoholic hydrogen chloride on potassium hydroxyphenylhydrazinesulphonate, *parahydroxyphenylhydrazine hydrochloride* is obtained, crystallising from water in colourless needles; it reduces Fehling's solution and ammoniacal silver nitrate in the cold. The *oxalate* crystallises in colourless leaflets. Attempts to prepare the free base have so far proved unsuccessful.

Nitrosoparahydroxyphenylhydrazine, formed by the action of nitrous acid on the hydrochloride, separates in small, brownish crystals and has the peculiar penetrating odour of nitrosophenylhydrazine. A. W. C.

Nitrosoalphylhydroxylamines. By EUGEN BAMBERGER (*Ber.*, 1898, **31**, 574—589).—When nitrosophenylhydroxylamine, $NO\cdot NPh\cdot OH$, is allowed to remain in benzene solution at 0° or at the ordinary temperature, it decomposes; gas is evolved, consisting chiefly of nitrogen, but containing also carbonic anhydride and a little nitric oxide; a solid deposit is gradually formed, which at first is mainly diazobenzene nitrate, but afterwards contains dipara- and orthopara-dinitrodiphenylamine, paranitrodiphenylamine, and in one case the nitrosamine of the last substance; the mother liquor is found to contain nitrosobenzene and phenol. The diparanitrodiphenylamine is the main product, and the reaction in question even affords a convenient method of preparing it. The diazobenzene nitrate and phenol, and the nitrosobenzene are doubtless secondary products due to the

action of nitrous acid on the nitrosophenylhydroxylamine, for a special experiment showed that the reaction between these two substances results in the formation of diazobenzene nitrate together with a little nitrosobenzene. Nitrosophenylhydroxylamine, or, rather its potassium salt, is reduced by sodium amalgam at 0° to the isodiazotate and, in part, to phenylhydrazine, but no normal diazotate is formed; nitrosoparatolylhydroxylamine behaves in precisely the same manner. Potassium permanganate oxidises the potassium salt of nitrosophenylhydroxylamine at 0° to nitrosobenzene and potassium nitrite; the same product is obtained when sodium hypochlorite is used as the oxidising agent.

Nitrosophenylhydroxylamine can be converted into the methylic ether by treating its potassium salt with methyl alcoholic, or its silver salt with ethereal, methylic iodide, as well as by treating the hydroxylamine itself with diazomethane in ethereal solution (Abstr., 1897, i, 40). In all cases, the same oxygen-ether is obtained; in this paper, it is formulated as O:NPh:N·OMe, whereas in the former paper equal, if not greater, prominence was given to the formula $O<\begin{matrix}NPh\\ | \\ N\cdot OMe\end{matrix}$. This ether, in moist ethereal solution, is reduced by aluminium amalgam at a temperature below 0° to diazobenzene methylic ether, NPh:N·OMe; by zinc dust in aqueous alcoholic solution containing ammonium acetate, as well as in dilute acetic acid solution, to diazonium acetate; and by sodium amalgam in aqueous alcoholic solution, to phenylhydrazine. It is hydrolysed by aqueous methyl alcoholic potash, and by aluminium chloride in benzene solution, nitrosophenylhydroxylamine being formed.

Nitrosoparabromophenylhydroxylamine, $C_6H_4Br\cdot N(NO)\cdot OH$, is obtained by adding sodium nitrite to a cooled solution of parabromophenylhydroxylamine in aqueous alcoholic hydrochloric acid; it melts at 81—82°; its *potassium* and *silver* salts were prepared. By treatment of the latter with methylic iodide, as well as from the hydroxylamine itself with diazomethane, the *methylic ether* was obtained; this melts at 84·5—85·5°, and is volatile with steam. In its properties, it resembles the compound containing no bromine; it does not give the Liebermann nitroso-reaction; it is so stable that it crystallises unchanged from a hot solution of potassium dichromate and sulphuric acid; it is reduced by aluminium amalgam to parabromodiazobenzene methylic ether, and by sodium amalgam to parabromophenylhydrazine, and it is hydrolysed by aqueous methyl alcoholic potash to nitrosoparabromophenylhydroxylamine. C. F. B.

Iodine Substitution Products of some Aromatic Alcohols, Aldehydes, and Acids. By JOHANNES SEIDEL (*J. pr. chem.*, 1898, 57, 204—206).—When an alcoholic solution of saligenin is treated with iodine in the presence of mercuric oxide, a mixture of the mono- and di-iodo-derivatives is obtained, which can be separated by means of the difference in their solubilities in warm sodium hydroxide, and purified by recrystallisation from water.

Iodosaligenin forms glistening leaflets melting at 138° and the *di-iodo*-derivative needles melting at 106°.

Di-iodosalicylaldehyde, obtained in a manner similar to the above, melts at 108°; its *phenylhydrazone* crystallises from acetic acid in yellow needles melting at 167·5°; its *hydrazone* forms small, yellow granules, decomposing without melting at 200°; its *oxime*, small, white needles, decomposing without melting at 210°, and its *condensation products* with aniline and paratoluidine crystallise from alcohol in orange-yellow needles, both melting at 147·5°. Iodosalicylaldehyde could not be obtained in a pure state.

Di-iodoparahydroxybenzaldehyde forms white needles melting and decomposing above 190°; the *oxime* crystallises in small, white needles melting and decomposing at 210°; the *phenylhydrazone*, yellow needles melting at 159°; the *anilide*, beautiful, dark violet plates melting at 166°; the *paratoluidide*, steel-blue leaflets melting at 190°, whilst the *paranitranilide* forms a red, crystalline powder melting and decomposing at 210°. No condensation product could be obtained with orthonitraniline.

No iodine derivatives of anisaldehyde could be obtained when using the above method, but on heating under pressure with iodine and iodic acid, *iodanisaldehyde* melting at 107—108° is obtained, together with a large amount of iodanisic acid; the latter is being further investigated, as also is the action of iodine on coumarin under varying conditions. A. W. C.

The Silver Salt of 4-Nitro-2-amidobenzoic Acid and its Behaviour with Alkylic and Acidyl Haloids. By HENRY L. WHEELER and BAYARD BARNES (*Amer. Chem. J.*, 1898, **20**, 217—222).—4-*Nitro-2-acetamidobenzoic acid*, prepared by oxidising 4-nitro-2-acetotoluidide with 1 per cent. potassium permanganate, crystallises from alcohol in pale yellow needles, melts at about 215°, and is converted into its *sodium* salt, a bright yellow powder, by adding sodium ethoxide to its alcoholic solution; the *silver* salt is a yellow powder, which is not affected by light.

Curtius (Abstr., 1884, 1306) has prepared the ethylic and methylic salts of acetamidoacetic acid by treating the silver salt of the latter with ethylic or methylic iodide respectively. The authors find similarly that when either of the salts described above is heated with ethylic iodide in a sealed tube at 190°, *ethylic 4-nitro-2-acetamidobenzoate* is formed, which crystallises from alcohol or light petroleum in bright yellow plates or flattened prisms, and melts at 112°; cold sodium hydroxide converts this into sodium 4-nitro-2-acetamidobenzoate, whilst alcoholic sulphuric acid removes the acetyl group only. 4-*Nitro-2-amidobenzoic acid* crystallises from alcohol in bright red needles, and, when heated, darkens at 260°, and melts and decomposes at 264°. The *ammonium* salt is readily soluble in water, and the same is true of the *sodium* salt although it is sparingly soluble in alcohol; the *silver* salt is a pinkish powder which darkens on being heated; the *methylic* salt, prepared by boiling the acid with methylic alcohol and sulphuric acid, crystallises from alcohol or light petroleum in dark-orange needles, and melts at 157°; the *ethylic* salt forms dark-orange plates and is easily soluble in alcohol and benzene.

On heating silver 4-nitro-2-amidobenzoate with acetic chloride, the

acetyl derivative of the acid is alone obtained, no mixed anhydride being formed; silver anthranilate behaves similarly under the same conditions.

Silver 4-nitro-2-amidobenzoate, on being heated during three days with ethylic iodide, is converted into a mixture of 4-*nitro*-2-*ethyl amidobenzoic acid* and its *ethylic* salt; the former crystallises from alcohol and benzene in golden-yellow plates, and melts at 223°, whilst the latter, which is formed in smaller quantity, separates in pale yellow needles and melts at 80°. The action is therefore analogous to that of ethylic iodide on the alkali salts of the amidobenzoic acids.

W. A. D.

Synthesis of 3-Hydroxyflavone. By T. Emilewicz and Stanislaus von Kostanecki (*Ber.*, 1898, **31**, 696—705).—2-Acetoxybenzylideneacetophenone dibromide reacts with alcoholic potash, yielding α-coumaryl phenyl ketone, $C_6H_4<\substack{-O-\\ CH}>C\cdot COPh$, (Abstr., 1896, i, 239). *Benzylidene-resacetophenone monethylic ether*,

$$OEt\cdot C_6H_3(OH)\cdot CO\cdot CH\colon CHPh,$$

is obtained in the form of its sodium derivative when resacetophenone monethylic ether (10 grams) and benzaldehyde (5·9 grams) are dissolved in alcohol, and 50 per cent. sodium hydroxide (20 grams) is added to the warm solution, the whole being kept in a warm place for some time. The free monethylic ether is precipitated on the addition of dilute acid, and, after recrystallisation from alcohol, forms yellow needles melting at 104°; it is insoluble in cold aqueous alkalis, and is decomposed by boiling sodium hydroxide solution. Its *acetyl* derivative crystallises in yellow needles melting at 74—75°, and yields a *dibromide* crystallising in needles and melting at 118—119°. When the alcoholic solution of this dibromide is treated with potassium hydroxide, 3-*ethoxyflavone*, $OEt\cdot C_6H_3<\substack{O-CPh\\ CO\cdot CH}$, is formed; this crystallises from alcohol, or, still better, from benzene, in needles melting at 138—139° and does not resemble Brüll and Friedländer's 3-methoxyflavone (Abstr., 1897, i, 221), which is in reality 3-methoxybenzylidene coumaranone. Brüll and Friedländer's compound yields a yellow solution with sulphuric acid, whereas ethoxyflavone gives a pale blue solution with an extremely characteristic blue fluorescence. When fused with potash according to Piccard's method, ethoxyflavone yields acetophenone, resacetophenone monethylic ether, resacetophenone, resorcinol, and benzoic acid. When boiled with concentrated sodium ethoxide solution, it is decomposed quantitatively into resacetophenone monethylic ether and benzoic acid.

3-*Hydroxyflavone*, which is obtained when the ethoxy-derivative is boiled for several hours with hydriodic acid (1·7), is best separated from any of the unaltered compound by the aid of dilute sodium hydroxide; it crystallises from alcohol in colourless needles melting at 240°; its solutions in alkalis are of a pale yellow colour and exhibit no fluorescence, whereas its sulphuric acid solution is colourless and has a strong blue fluorescence. Its *acetyl* derivative crystallises in colourless needles melting at 129—130°.

Piperonal-resacetophenone monethylic ether,

$$\overset{4}{\mathrm{OEt}}\cdot \mathrm{C_6H_3}\overset{2}{(\mathrm{OH})}\cdot \overset{1}{\mathrm{CO}}\cdot\mathrm{CH\colon CH}\cdot \overset{1}{\mathrm{C_6H_3}}<\overset{3}{\underset{4}{\substack{\mathrm{O}\\ \mathrm{O}}}}>\mathrm{CH_2},$$

obtained from piperonal and resacetophenone monethylic ether in the presence of strong alkali, crystallises in large yellow or orange coloured plates and melts at 160°; it is insoluble in aqueous alkalis, and on boiling with sodium hydroxide solution is decomposed. Its *acetyl* derivative crystallises in yellow needles melting at 100—101°, and yields a *dibromide* crystallising in colourless needles and melting at 130°. The dibromide, when treated with alcoholic potash, yields a *compound*, $C_{18}H_{14}O_5$. J. J. S.

Synthesis of Flavone Derivatives. By W. Feuerstein and Stanislaus von Kostanecki (*Ber.*, 1898, **31**, 710—719.)—*Phenacylideneflavene*, $C_{23}H_{16}O_2$, obtained when 2-hydroxybenzylidenediacetophenone is boiled for a short time with 10 per cent. hydrochloric acid, crystallises from alcohol, in which it is fairly readily soluble, in intensely yellow needles melting at 131°; the crystals are coloured orange by concentrated sulphuric acid, and the acid solution has a yellow colour and blue fluorescence. 2-*Bromophenacylideneflavene*, $C_{23}H_{15}BrO_2$, is obtained in a similar manner from Cornelson and Kostanecki's 5-bromo-2-hydroxybenzylidenediacetophenone; it is advisable, however, to add a small quantity of alcohol to facilitate the reaction. It crystallises in reddish-yellow needles, melts at 169—170°, is turned orange coloured by sulphuric acid, in which it dissolves, giving a yellow solution with a green fluorescence. Parahomosalicylaldehyde yields two condensation products with acetophenone. When Bablich and Kostanecki's method (Abstr., 1896, i, 239) is employed, 2-*Hydroxy*-5-*methylbenzylideneacetophenone*, $OH\cdot C_6H_3Me\cdot CH\colon CH\cdot COPh$, is the chief product; it crystallises from alcohol in yellow plates, melts and decomposes at 146°, dissolves in dilute sodium hydroxide solution, and, on the addition of concentrated alkali, a yellowish-red *sodium* derivative crystallises out. Its *acetyl* derivative, obtained by the action of acetic anhydride and dry sodium acetate, crystallises in long, yellowish, glistening prisms.

When parahomosalicylaldehyde (1 mol.) reacts with acetophenone (2 mols.) in the presence of an excess of sodium hydroxide (Abstr., 1896, i, 240), the chief product is 2-*hydroxy*-5-*methylbenzylidenediacetophenone*, $OH\cdot C_6H_3Me\cdot CH(CH_2COPh)_2$, which crystallises from alcohol in short, colourless prisms melting at 151°. When boiled with hydrochloric acid, it yields 2-*methylphenacylideneflavene*, $C_{23}H_{15}MeO_2$, which crystallises in thin, glistening, yellow needles melting at 156—157°. 4′ : 4″-*Dimethylphenacylideneflavene*, $C_{23}H_{14}Me_2O_2$, obtained from 2-hydroxybenzylidenebismethyl paratolyl ketone, crystallises from alcohol in reddish-yellow needles melting at 145°.

Bromosalicylaldehyde (COH : OH : Br = 1 : 2 : 5) reacts with paratolyl methyl ketone, yielding 5-*bromo*-2-*hydroxybenzylidenemethyl paratolyl ketone*, $OH\cdot C_6H_3Br\cdot CH\colon CH\cdot CO\cdot C_6H_4Me$, which crystallises in yellow needles melting and decomposing at 196°, and 5-*bromo*-2-*hydroxybenzylidenebismethyl paratolyl ketone*, $OH\cdot C_6H_3Br\cdot CH(CH_2\cdot CO\cdot C_6H_4Me)_2$, crystallising in colourless plates and melting at 158°. The two compounds are readily separated by the aid of warm sodium hydroxide

solution, in which the former compound is readily soluble. 5-*Bromo*-2-*acetoxybenzylidenemethyl paratolyl ketone*,

$$OAc\cdot C_6H_3Br\cdot CH\colon CH\cdot CO\cdot C_6H_4Me,$$

melts at 153°. 2-*Bromo*-4′:4″-*dimethylphenacylideneflavene* crystallises in yellow needles melting at 176—177°.

These phenacylideneflavene derivatives are stable towards aqueous potash, but are readily hydrolysed by sodium ethoxide. When phenacylideneflavene (10 grams) was heated for several hours on the water bath with 20 grams of sodium dissolved in 200 grams of alcohol, the products isolated were acetophenone, orthohydroxyacetophenone, and benzoic acid. *Orthohydroxyacetophenone* is a colourless oil boiling at 218°; it yields a sparingly soluble yellow *sodium* derivative, gives a violet coloration with ferric chloride, and reacts with an alcoholic solution of benzaldehyde in the presence of sodium hydroxide, yielding 2′-*hydroxybenzylideneacetophenone*, $OH\cdot C_6H_4\cdot CO\cdot CH\colon CHPh$, which crystallises in yellow needles melting at 88—89°. It dissolves slowly in cold sodium hydroxide, readily when gently warmed, and is decomposed when boiled with the alkali. 2-Bromophenacylideneflavene, when hydrolysed in a similar manner, yields acetophenone, benzoic acid, and 5-*bromorthohydroxyacetophenone*; the latter crystallises from alcohol in colourless needles, melts at 61—62°, yields a sparingly soluble, crystalline *sodium* derivative, and reacts with benzaldehyde in the presence of 50 per cent. sodium hydroxide solution, yielding 5′-*bromo*-2′-*hydroxybenzylideneacetophenone*, which crystallises from alcohol in pale yellow needles melting at 107—108°.

The hydrolysis of phenacylideneflavene above described agrees with the constitution, $\begin{matrix} CPh\colon CH \\ | \\ O{-}C_6H_4 \end{matrix}\!\!>\!C\colon CH\cdot COPh$, which the authors suggest.

In the formation of phenacylideneflavene from hydroxybenzylidenediacetophenone, acetophenone is always formed, together with another substance, which the authors have proved to be 2-*hydroxybenzylacetophenone*, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COPh$; this crystallises in colourlesss plates melting at 91—92°, and its *acetyl* derivative crystallises in colourless needles and melts at 65—66°. 5-*Bromo*-2-*hydroxybenzylacetophenone*, a bye-product obtained in the preparation of 2-bromophenacylideneflavene, melts at 94—95°, and its *acetyl* derivative at 67°.

J. J. S.

Hydroxybenzylidenebromindanones. By W. KLOBSKI and STANISLAUS VON KOSTANECKI (*Ber.*, 1898, **31**, 720—726).—Von Miller and Rodhe's 2-bromindanone (Abstr., 1890, 1139) is best prepared by adding parabromophenylpropionic acid to sulphuric acid previously heated to 145°; the temperature, which falls slightly, is again brought to 145°, and when cold the mixture is poured into water.

2-*Bromobenzylideneindanone*, $C_6H_3Br{<}\begin{matrix}CH_2\\CO\end{matrix}{>}C\colon CHPh$, is obtained when 10 per cent. aqueous sodium hydroxide is added to a warm alcoholic solution of the above compound and benzaldehyde; it crystallises in small, colourless, glistening needles melting at 162—163°, and dissolves in concentrated sulphuric acid, yielding an intense yellow solution.

The three hydroxybenzaldehydes also react with bromindanone in the presence of alkali; the yields in the cases of the ortho- and meta-compounds are good, but with the para-compound a considerable amount of a substance which is insoluble in alkali is formed. Other hydroxyaldehydes which have a hydroxy-group in the para-position, react in the same manner as parahydroxybenzaldehyde. Such aldehydes, however, react readily with bromindanone when alcoholic solutions of the aldehyde and indanone derivative are boiled with fuming hydrochloric acid.

2-*Bromo-2'-hydroxybenzylideneindanone*,

$$C_6H_3Br{<}{}^{CH_2}_{CO}{>}C{:}CH\cdot C_6H_4\cdot OH,$$

is obtained in the form of its sparingly soluble *sodium* derivative when a warm alcoholic solution of equivalent quantities of salicylaldehyde and bromindanone is treated with 50 per cent. sodium hydroxide (twice the weight of the aldehyde employed). The free hydroxybromobenzylideneindanone crystallises in glistening, yellow needles which carbonise at about 220°; its sulphuric acid solution has an orange colour. The *acetyl* derivative,

$$C_6H_3Br{<}{}^{CH_2}_{CO}{>}C{:}CH\cdot C_6H_4\cdot OAc,$$

crystallises in colourless needles melting at 142°.

2-*Bromo-3'-hydroxybenzilideneindanone* crystallises from alcohol in long, glistening needles melting at 239°, and yields an *acetyl* derivative crystallising in colourless plates and melting at 173—174°.

2-*Bromo-4'-hydroxybenzilideneindanone* crystallises in minute, pale yellow needles melting at 252°; its solution in sodium hydroxide has a reddish-yellow colour, and its solution in concentrated sulphuric acid a yellow colour. Its *acetyl* derivative, which is very sparingly soluble in hot alcohol, crystallises from glacial acetic acid in colourless needles melting at 226—227°.

2-*Bromo-3' : 4'-dihydroxybenzylideneindanone*, obtained from protocatechuic aldehyde and bromindanone by the aid of fuming hydrochloric acid, crystallises from alcohol in brownish-yellow needles melting at 279—280°; its sodium hydroxide solution is purple, and its sulphuric acid solution yellow. It is a dye, its alumina lake having a yellow to pale orange colour, whereas the alumina lake of 4' : 4'-dihydroxybenzylideneindanone is red. The *diacetyl* derivative crystallises from glacial acetic acid in needles melting at 153°.

2-*Bromo-4'-hydroxy-3'-methoxybenzylideneindanone*,

$$C_6H_3Br{<}{}^{CH_2}_{CO}{>}C{:}CH\cdot C_6H_3(OMe)\cdot OH,$$

from vanillin and bromindanone, crystallises in large, yellow needles melting at 254—255°, and yields a sparingly soluble *sodium* derivative. Its *acetyl* derivative melts at 201—202°.

2-*Bromo-3'-4'-dihydroxybenzylideneindanone methylenic ether*,

$$C_6H_3Br{<}{}^{CH_2}_{CO}{>}C{:}CH\cdot C_6H_3{<}{}^{O}_{O}{>}CH_2,$$

obtained from the action of piperonal on benzaldehyde in the presence of dilute alkali, crystallises from a mixture of acetic acid and alcohol

in glistening, straw-yellow needles melting at 223—224°; its sulphuric acid solution has a bright, cherry red colour.

These bromhydroxybenzylideneindanones differ from the simple hydroxybenzylideneindanones in their stability towards alkalis, and resemble more the hydroxybenzylidenecoumarones. All three groups of compounds resemble one another in their colour reactions; hydroxybenzylideneacetophenones also give similar colorations with sulphuric acid. All these compounds contain the double chromophore CO·C:C.

J. J. S.

2-Hydroxydibenzylideneacetone. By STANISLAUS VON KOSTANECKI and D. MARON (*Ber.*, 1898, 31, 726—730).—Haller and Kostanecki (this vol., i, 201) have already shown that compounds containing the chromophore CO·C:C·C:C are more deeply coloured than those with the simpler chromophore, CO·C:C. Experiments have been made to see whether this is also true of the complex chromophore C:C·CO·C:C, but no definite conclusions can be deduced from the results obtained.

Benzylidenepiperonalacetone, $CHPh:CH\cdot CO\cdot CH:CH\cdot C_6H_3<^{O}_{O}>CH_2$, obtained from piperonal and benzylideneacetone, or from benzaldehyde and piperonalacetone by Claisen and Ponder's method, melts at 115°; it dissolves in concentrated sulphuric acid, yielding a magenta-coloured solution, and, on the addition of water, a dark-coloured, flocculent precipitate is thrown down.

2-*Hydroxydibenzylideneacetone*, $OH\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH:CHPh$, is obtained when 2-hydroxybenzylideneacetone (10 grams) and benzaldehyde (6·5 grams) are dissolved in 130 grams of alcohol, the solution treated with 10 per cent. sodium hydroxide (100 grams), and at the end of 24 hours poured into dilute hydrochloric acid; it crystallises from benzene in yellow plates, and has the same melting point as 2-hydroxybenzylacetone (139°). Its alkali solutions are coloured reddish-yellow, as is also its solution in concentrated sulphuric acid; the addition of water to the latter gives a red precipitate. Its *acetyl* derivative crystallises from alcohol in pale yellow needles melting at 72—73°. The alkali solutions of 2-hydroxydibenzylideneacetone are deeper coloured than those of 2-hydroxybenzylideneacetophenone, or of 2′-hydroxybenzylideneacetophenone, probably owing to the fact that it contains the chromophore C:C in addition.

2-*Hydroxybenzylidenepiperonalacetone*,

$$OH\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH:CH\cdot C_6H_3<^{O}_{O}>CH_2,$$

crystallises from benzene in small, yellow crystals, melts at 168°, dissolves in alkalis, yielding yellowish-red solutions, and in concentrated sulphuric acid giving a reddish-purple solution; its *acetyl* derivative crystallises in amber-yellow crystals melting at 144—145°.

2-*Ethoxybenzylidenepiperonalacetone* crystallises from alcohol in yellow needles melting at 90°.

J. J. S.

α-Naphthaflavone. By STANISLAUS VON KOSTANECKI (*Ber.*, 1898, 31, 705—709).—2-*Benzylideneacetyl*-1-*naphthol*, $OH\cdot C_{10}H_6\cdot CO\cdot CH:CHPh$, is obtained as a red precipitate when 2-aceto-1-naphthol (10 grams),

benzaldehyde (6 grams), and warm alcohol (100 grams) are treated with 50 per cent. sodium hydroxide (20 grams) and the mixture warmed for an hour on the water bath and then poured into cold water; it crystallises from alcohol in orange-coloured plates, melts at 125—126°, and dissolves in concentrated sulphuric acid to a yellowish-red solution. Its *acetyl* derivative crystallises from dilute alcohol in yellow plates, melts at 95—96°, and yields a *dibromide* crystallising from a mixture of alcohol and benzene in colourless needles melting at 186—187°.

a-Naphthaflavone, $C_{10}H_6<\begin{matrix}O-CPh\\CO\cdot CH\end{matrix}$, is obtained when the above dibromide is suspended in alcohol and 30 per cent. potassium hydroxide (3 mols.) is added, the mixture well shaken, the clear solution poured into water and the precipitate thus obtained crystallised several times from alcohol. It forms pale yellow plates melting at 154—156°, and dissolves in concentrated sulphuric acid, yielding a yellow solution with a green fluorescence. When hydrolysed by boiling with concentrated sodium ethoxide, it yields 2-acetyl-1-naphthol and benzoic acid.

2-*Piperonalacetyl*-1-*naphthol*, $OH\cdot C_{10}H_6\cdot CO\cdot CH:CH\cdot C_6H_3<\begin{matrix}O\\O\end{matrix}>CH_2$, crystallises from a mixture of acetic acid and alcohol in pale red needles melting at 154—155°; it is insoluble in aqueous alkalis, and its sulphuric acid solution has a red colour. Its *acetyl* derivative crystallises in orange-coloured needles melting at 129—130°, and yields a *dibromide* crystallising from a mixture of chloroform and ether in yellow crusts, which decompose at 160°. 3'-4'-*Dihydroxy-a-naphthaflavone methylenic ether*, $CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3\cdot C\leqslant\begin{matrix}O-C_{10}H_6\\CH\cdot CO\end{matrix}$, obtained by the action of potassium hydroxide on the dibromide, crystallises from its pyridine solution on the addition of alcohol in glistening, yellow needles, melting at 253—254°. It is sparingly soluble in alcohol, more readily in benzene or acetic acid; its alcoholic solution has a blue fluorescence. It dissolves in concentrated sulphuric acid, yielding a yellow solution with a feeble green fluorescence which disappears after some time. When hydrolysed with sodium ethoxide, it yields 2-acetyl-1-naphthol and piperonylic acid. J. J. S.

Ketones obtained from the Violet, and the Compounds of the Citral (Geranaldehyde) Series related to them. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1898, 31, 808—866. Compare Abstr., 1895, i, 530).—This paper summarises the investigations of the fragrant oil of dried iris root which have been carried on during the past five years. The greater part of the information relating to citral, geraniol, linalool, and geranic acid has already appeared.

Pseudoionone is the product of alkaline condensation of citral with acetone (Tiemann and Krüger, Abstr., 1894, i, 82). Under the influence of acids and of alkalis, it readily passes into the isomeric cyclic ketone ionone. The statement that it does not combine with hydrogen sodium sulphite is only true in the case of cold solutions, as, when boiled with the liquid, the ketone enters into combination; on liberating it from the product, it boils at 143—145° under a pressure of 12 mm.,

has the sp. gr. = 0·8984, and the refractive index $[n]_D = 1·53346$. Neither the oxime nor the phenylhydrazone is suited to the isolation of pseudoionone, difficulty being experienced in regenerating the ketone uncontaminated with ionone. The *semicarbazone* melts at 142° after recrystallisation from alcohol, benzene, and petroleum successively; it is very readily hydrolysed in alcoholic solution by an equivalent amount of sulphuric acid, yielding pseudoionone in a form which boils at 146—148° under a pressure of 12 mm., has the sp. gr. = 0·898, and the refractive index $[n]_D = 1·5274$. The *parabromophenylhydrazone* crystallises with difficulty, and after recrystallisation from petroleum melts at 102—104°; as the corresponding derivative of ionone crystallises very readily, a convenient method of detecting pseudoionone consists in acting on it with dilute acid, and preparing the bromophenylhydrazone of the ionone thus produced. A more rapid process for the detection of pseudoionone consists in transforming the ketone into β-ionone (following abstract) by the agency of concentrated sulphuric acid, and converting the product into the semicarbazone (m. p. 148°); a third method consists in converting the ketone by means of hydriodic acid into the hydrocarbon ionene, oxidising the latter to ioniregenetricarboxylic acid, and preparing the anhydride (m. p. 214°).

Pseudoionone is slowly oxidised by an ice cold 2 per cent. solution of potassium permanganate; on further oxidation of the filtrate with chromic acid, acetone, acetic, and levulinic acids are produced (compare Abstr., 1895, i, 646). In consideration of this behaviour, the author represents the constitution of pseudoionone by the formula $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}COMe$ (compare Abstr., 1894, i, 82).

Methods of detecting ionone are described (compare Tiemann and Krüger, Abstr., 1895, i, 530), and the constitution of this substance is discussed; reasons are given in detail for ascribing to it the constitutional formula $\begin{array}{l}CH_2{\cdot}CMe_2{\cdot}CH{\cdot}CH{:}CH{\cdot}COMe \\ CH_2{\cdot}CH{=}CMe\end{array}$ (compare Abstr., 1894, i, 83).

Hydroxyionolactone, $\begin{array}{l}CH_2{\cdot}CMe_2{\cdot}CH\text{——}CO \\ |\qquad\qquad\qquad >CMe{\cdot}OH\ | \\ CH_2\text{——}CH\text{——}O\end{array}$, is prepared by oxidising ionone with potassium permanganate; it is sparingly soluble in water, from which it crystallises, melting at 130°. The lactone is very unstable, and quickly becomes yellow when exposed to air; it gradually dissolves in caustic soda, but is reprecipitated on adding an acid. Treatment with hydrogen bromide converts it into the *bromolactone*, $C_{10}H_{15}BrO_2$, and when this is boiled with caustic alkali, it yields a dihydroxydihydrocyclogeranic acid melting at 177·5° (compare Tiemann and Semmler, Abstr., 1894, i, 85).

Geronic (4-*dimethylheptan*-6-*onoic*) *acid*,

$$COMe{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

which is also a product of the oxidation of ionone with potassium permanganate, is a colourless, viscous oil. The *semicarbazone* melts at 164°. Alkali hypobromite eliminates bromoform from geronic acid, giving rise to asymmetrical β-dimethyladipic acid.

In addition to hydroxyionolactone and geronic acid, asymmetrical

α-dimethylglutaric and asymmetrical dimethylsuccinic acids are produced by the oxidation of ionone. The formation of these substances is in agreement with the above expression of the constitution of ionone. M. O. F.

Resolution of Ionone into Two Structurally Identical Forms, α-Ionone and β-Ionone. By J. C. W. Ferdinand Tiemann (*Ber.*, 1898, 31, 867—881. Compare Abstr., 1895, i, 530).—Ionone is the ketone obtained by Tiemann and Krüger on heating pseudoionone with dilute sulphuric acid and a small quantity of glycerol (Abstr., 1894, i, 82). Employing concentrated sulphuric acid, de Laire obtained ionone in a form which scarcely differed from ordinary ionone in physical characteristics, but which yielded different derivatives with substituted ammonias (American Patent, No. 600429, 1898). The isomeride, which has been referred to as isoionone, is structurally identical with ionone, and probably differs from it in some stereochemical respect, depending on the disposition of the ·CH:CH·COMe group in the formula $\begin{matrix} CH_2\cdot CMe_2\cdot CH\cdot CH{:}CH\cdot COMe \\ | \qquad\qquad\quad | \\ CH_2\cdot CH{=\!=}CMe \end{matrix}$ for ionone. The two modifications of the ketone are now distinguished as α-ionone and β-ionone.

α-Ionone is prepared from commercial ionone by converting it into the oxime, crystallising this derivative from petroleum, and regenerating the ketone with dilute sulphuric acid; it boils at 123—124°, and 134—136° under pressures of 11 mm. and 17 mm. respectively. It has the sp. gr. = 0·932, and the refractive index $[n]_D = 1·4980$, whence the molecular refraction is 60·38; the value calculated for the formula $C_{13}H_{20}O$, with two ethylenic linkings, is 59·24. In certain respects the odour of α-ionone differs slightly from that of the isomeride. The *oxime* crystallises when the solution in low-boiling point petroleum is cooled with a freezing mixture; the derivative of β-ionone does not separate, and consequently may be removed from the isomeric substance. The oxime melts at 89—90°. The *semicarbazone* dissolves more readily than β-ionone semicarbazone in petroleum; it melts at 107—108° (compare Abstr., 1895, i, 530). The *parabromophenylhydrazone* crystallises readily from glacial acetic acid, and from methylic and ethylic alcohols; it softens at 135°, and melts at 142—143°. *α-Iononeoximeacetic acid*, $C_{13}H_{20}{:}N\cdot O\cdot CH_2\cdot COOH$, is prepared from the oxime and chloracetic acid; it crystallises from petroleum, and melts at 98—99°. *α-Iononehydrazone*, $C_{13}H_{20}{:}N\cdot N{:}C_{13}H_{20}$, melts at 99°. Both α-ionone and β-ionone, when oxidised with potassium permanganate, yield the same products as ionone (preceding abstract), namely, hydroxyionolactone, geronic acid, asymmetrical β-dimethyladipic acid, and asymmetrical α-dimethylglutaric acid. Furthermore, the hydrocarbon ionene, obtained by the action of hydriodic acid on the ketone, differs in no respect from ionene prepared from β-ionone.

β-Ionone is obtained from the mixture of ketones by means of the semicarbazone, which crystallises more readily than the corresponding derivative of the α-ketone; it boils at 127—128·5°, 134·5—135·5°, and 140°, under pressures of 10 mm., 14·5 mm., and 18 mm. respectively.

It has the sp. gr. = 0·946, and the refractive index $[n]_D = 1·521$, whence the molecular refraction is 61·70. The *oxime* is an oil, but yields the *oximeacetic acid*, which crystallises from petroleum in leaflets, and melts at 103°. The *semicarbazone* melts at 148—149°, and becomes yellow on exposure to air. The *parabromophenylhydrazone* crystallises from petroleum in large, rectangular plates, and melts at 115—116°; whilst the *hydrazone* separates from alcohol in shortened, rhombic prisms, and melts at 104—105°. M. O. F.

Constitution of Isogeranic (Cyclo-Geranic) Acid. Isogeranionitrile. By J. C. W. FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1898, **31**, 881—890. Compare Tiemann and Semmler, Abstr., 1894, i, 85).—By studying the products of oxidation of isogeranic acid, the authors have shown that this compound has the constitution expressed by the formula $\begin{matrix} CH_2\cdot CMe_2\cdot C\cdot COOH \\ | \qquad\qquad\quad \| \\ CH_2\cdot CH_2—CMe \end{matrix}$; dihydroxydihydroisogeranic acid (*loc. cit.*), therefore, has the constitution

$$\begin{matrix} CH_2\cdot CMe_2\cdot C(OH)\cdot COOH \\ | \qquad\qquad | \\ CH_2\cdot CH_2—CMe\cdot OH \end{matrix}.$$

Isogeronic (2-*dimethylheptan*-6-*onoic*) *acid*,

$$OMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot COOH,$$

is produced from isogeranic acid by further oxidising with chromic acid the products obtained by oxidising geranic acid with potassium permanganate; it is a viscous, colourless oil, which dissolves readily in water, alcohol, and ether. The *semicarbazone* is almost insoluble in ethylic acetate, but crystallises from alcohol in leaflets and melts at 198°. Oxidation of isogeronic acid with alkaline hypobromite eliminates one methyl group, giving rise to *unsymmetrical α-dimethyladipic acid*, which crystallises from benzene in needles, and melts at 87°; its *silver* salt is somewhat soluble in boiling water. The remaining products of oxidation of isogeranic acid are unsymmetrical α-dimethylglutaric and α-dimethylsuccinic acids.

The authors refer to the paper of Barbier and Bouveault on isogeranionitrile (Abstr., 1897, i, 537). M. O. F.

A Resinous Substance from Beetroot Juice. By EDMUND O. VON LIPPMANN (*Ber.*, 1898, **31**, 674—678).—The author describes an acid which he obtained in the form of a calcium salt when the juice from certain beetroots was passed over animal charcoal. In many respects it resembles Andrlik and Votoček's compound (*Zeit. Zuckerind. Böhm.*, **20**, 248). Neither the acid nor its calcium salt could be obtained in a crystalline form, and they were not analysed. When oxidised with nitric acid, it yields isophthalic acid; when fused with potash, the chief product is protocatechuic acid, and on boiling with alkali or barium hydroxide, it yields caffeic acid. J. J. S.

Ouabain. By ALBERT ARNAUD (*Compt. rend.*, 1898, **126**, 346—349). —Ouabain, when crystallised from aqueous solutions, can form three different hydrates, according to the temperature at which crystallisation takes place. The hydrate, $C_{30}H_{46}O_{12} + 9H_2O$, forms between 10° and 20°, and crystallises in quadratic tables, in which, according to Wyrouboff, $[a:c:1:1·6003]$.

The hydrate that forms at about 30° contains $4H_2O$, and that which is formed at about 60° contains $3H_2O$. The rotatory power of ouabain in aqueous solution is $[\alpha]_D = -30 \cdot 6°$. 100 c.c. of water dissolve, at 8°, 0·66 gram of ouabain; at 14·5°, 0·93 gram, and at 30°, 1·57 grams. Cryometric observations with aqueous and acetic acid solutions confirm the molecular weight previously attributed to the compound.

When hydrolysed with dilute acids, ouabain yields rhamnose and a red resin, which is doubtless a product of the polymerisation of the second product of the hydrolysis. Each molecule of ouabain yields one molecule of rhamnose. Emulsin, diastase and other soluble ferments have no action on ouabain, but certain microbes seem to be able to split it up into rhamnose and a crystalline product.

Concentrated nitric acid converts ouabain into amorphous nitro-derivatives, large quantities of oxalic acid being formed if the liquid is heated. Dilute nitric acid yields crystallisable nitro-derivatives, which seem to be acidic in character, and are probably derived from the second product of hydrolysis. Bromine yields an amorphous derivative containing nearly 63 per cent. of the halogen. Alkalis form, with ouabain, compounds which are extremely soluble and are not crystallisable. Sodium and potassium in presence of alcohol yield compounds which seem to be of the type $C_{30}H_{45}MO_{12}$, and with an excess of the metals more hydrogen is displaced. Acetic anhydride between 30° and 70° yields an acetin, $C_{30}H_{39}O_{12}Ac_7$, which crystallises in micaceous lamellæ melting at 270—275°. C. H. B.

Compounds from Lichens. By OSWALD HESSE (*Ber.*, 1898, 31, 663—665. Compare Abstr., 1897, i, 630).—*Rhizocarpic acid* has the formula $C_{28}H_{22}O_7$ (compare Zopf, Abstr., 1895, i, 297), and can readily be separated from parellic acid and rhizonic acid which accompany it in *Rhizocarpon geographicum f. contiguum*. *Rhizonic acid*, $C_{19}H_{20}O_7$, forms prisms which are almost cubical, and melts and decomposes at 185°; when boiled with aqueous baryta, it yields carbonic anhydride, betorcinol and *rhizoninic acid*, $C_{10}H_{12}O_4$, which has the constitution of a *methylbetorcinolcarboxylic acid*, $OH \cdot C_8H_7(OMe) \cdot COOH$. In a previous paper (Abstr., 1897, i, 255) ethylic hæmatommate is erroneously included among the naturally occurring derivatives of betorcinol instead of methylic betorcinolcarboxylate. A. H.

The Lignone Colouring Matters and Cœrulignone. By CARL LIEBERMANN and GUSTAV CYBULSKI (*Ber.*, 1898, 31, 615—621).—When cœrulignone is treated with acids, derivatives of the colourless hydro-derivative are formed. A methyl alcoholic solution of hydrogen chloride converts it into *chlorhydrocœrulignone*,

$$OH \cdot C_6H_2(OMe)_2 \cdot C_6HCl(OMe)_2 \cdot OH,$$

which crystallises in small, colourless needles and melts at 141°. When ethylic alcohol is employed, the methoxyl groups are replaced by ethoxyl and *monochlorhydroethylcedriret*,

$$OH \cdot C_6H_2(OEt)_2 \cdot C_6HCl(OEt)_2 \cdot OH,$$

is produced which crystallises in colourless needles melting at 129—130° and yields a diacetyl-derivative which crystallises in colourless needles and melts at 94—96°. When this compound is treated with alcoholic ferric chloride, it is not converted into the corresponding quinone, but

yields a *compound* which forms small, red crystals melting at 159°, and probably has the constitution $OH \cdot C_6HCl(OEt)_2 \cdot C_6H_2(OEt) {<}^{O}_{O}$.

Aqueous hydrobromic acid converts cœrulignone into a mixture of hydrocœrulignone with brominated derivatives, whilst in alcoholic solution it yields a mixture of bromo- and dibromo-hydrocœrulignone. Acetic acid yields colourless hydrocœrulignone along with a dark brown oxidation product. The lignone colouring matters behave in a similar manner, but undergo change much more readily both in the presence of reducing agents and of acids. Thus the derivative of ψ-cumidine is converted by alcoholic sulphurous anhydride into *leucohexamethyl-lignone blue*, $C_{32}H_{36}N_2O_4$, which crystallises in colourless needles, and is reconverted into the colouring matter by exposure to the air or by treatment with ferric chloride. Dimethyl-lignone blue (derived from paratoluidine) is converted by methylic alcoholic hydrogen chloride into *leucochlorodimethyl-lignone blue*, $C_{28}H_{27}ClN_2O_4$, which is reconverted into the colouring matter by ferric chloride. The addition of acids to these quinonic substances therefore converts them into colourless compounds, and this explains the fact that the colouring matters themselves in alcoholic solution, and their sulphonic acids in aqueous solution, readily decompose, especially in the presence of an acid, and are, on this account, valueless for dyeing.

Dinitrodimethyl-lignone blue, $C_{28}H_{24}N_4O_8$, prepared from orthonitroparatoluidine, melts at 78—80°. *Methylenelignone blue*,

$$C_{14}H_{12}O_4 \Big< \begin{matrix} N \cdot C_6H_4 \\ N \cdot C_6H_4 \end{matrix} \Big> CH_2,$$

prepared from diparadiamidodiphenylmethane, is strongly hygroscopic.

A. H.

Phyllocyanic Acid and Phyllocyanates. By A. GUILLEMARE (*Compt. rend.*, 1898, **126**, 426—428.)—In order to prepare phyllocyanic acid, green leaves are treated at 90° with about one-quarter of their weight of sodium hydroxide solution of sp. gr. = 1·056. The liquid is saturated with carbonic anhydride, the upper part of the vessel being left full of this gas, and an excess of hydrochloric acid diluted with 100 vols. of water is added gradually, care being taken to avoid rise of temperature. The precipitated phyllocyanic acid is washed and is instantly and completely soluble, without decomposition, in a 1 per cent. solution of sodium or potassium hydroxide, or even ammonia. In order to purify it, the precipitate is treated with a dilute solution of an alkali carbonate in quantity insufficient to dissolve the whole of it, and this process may be repeated several times.

The properties of the compound thus obtained are identical with those of Fremy's phyllocyanic acid. The author has prepared, and will describe later, the phyllocyanates of the alkalis, alkali-earths, iron, aluminium, zinc, cadmium, copper, strontium, lead, mercury, silver, quinine, and cinchonine.

C. H. B.

Dihydropyrroline, Pyrrolidine, Tetrahydropyridine and Piperidine Derivatives. By ANDREAS LIPP (*Ber.*, 1898, **31**, 589—591.)—The author expresses surprise at the invasion of his

domain by Hielscher (this vol., i, 338) and Ladenburg (*ibid.*, 338, 339), and complains that the latter has misrepresented him in certain points. C. F. B.

Halogen Derivatives of Pyridine. By P. F. Trowbridge and O. C. Diehl (*J. Amer. Chem. Soc.*, 1897, 19, 558—575. Compare Abstr., 1896, i, 186 and 316, and this vol., i, 270).—*Pyridine hydriodide dibromide*, C_5NH_5,HI,Br_2, formed on passing carbonic anhydride saturated with bromine through an aqueous solution of pyridine hydriodide, crystallises from alcohol in reddish-brown plates and melts at 172—175°. *Pyridine methiodide dibromide*, C_5NH_5,MeI,Br_2, prepared similarly, crystallises from absolute alcohol in orange-yellow needles and melts at 61—62°; *pyridine ethiodide dibromide*, C_5NH_5,EtI,Br_2, separates from alcohol in orange-yellow crystals and melts at 25—26°.

When chlorine is passed into aqueous pyridine hydriodide, a *trichloride*, C_5NH_5,HI,Cl_3, of the latter is formed, which crystallises from alcohol and melts at 176°. *Pyridine methiodide tetrachloride*, C_5NH_5,MeI,Cl_4, prepared similarly, is a canary-yellow powder, which melts at 185°, and is probably identical with the substance formed on passing chlorine into a mixture of pyridine methochloride iodochloride, and potash (Bally, Abstr., 1888, 964). *Pyridine ethiodide tetrachloride*, C_5NH_5,EtI,Cl_4, melts at 123°.

The authors were unable to prepare the compound, $(C_5NH_5Br_2)_2,HBr$, obtained by Grimaux (Abstr., 1882, 1215) by acting on pyridine with bromine; on passing bromine vapours through a solution of pyridine in chloroform, *pyridine tetrabromide*, C_5NH_5,Br_4, separated. The latter melts at 58·5°, and on standing loses bromine and is converted into a *dibromide*, C_5NH_5,Br_2, which melts at 94—95°.

Pyridine hydrobromide forms colourless, transparent scales, and melts and decomposes at 200°. *Pyridine methobromide*, $C_5NH_5,MeBr + \frac{1}{2}H_2O$, prepared by passing methylic bromide through well-cooled pyridine, separates from alcohol in large crystals, and melts and partially decomposes at 135·5°; *pyridine ethobromide* obtained by warming pyridine with ethylic bromide, separates from alcohol in white crystals, and melts at 111—112°.

Iodine dissolved in alcohol or potassium iodide solution, displaces the bromine of pyridine hydrobromide, forming the pyridine hydriodide periodides described in a former paper (this vol., i, 270). Under the same conditions, pyridine methobromide yields the pentiodide, C_5NH_5,MeI,I_4, whilst from pyridine ethobromide an uncrystallisable product is obtained, which does not contain bromine and probably consists principally of the pentiodide, C_5NH_5,EtI,I_4.

A *perbromide*, $(C_5NH_5,HBr)_2Br_3$, is formed when an excess of bromine is aspirated through aqueous pyridine hydrobromide; it separates from alcohol in stable, dark-orange coloured crystals, melts at 125°, and is probably identical with the compound, $(C_5NH_5Br_2)_2,HBr$, described by Grimaux (*loc. cit.*) as formed by the action of bromine on pyridine, although the latter is stated to be unstable and to melt at 126°. When less bromine is used, pyridine hydrobromide gives rise to a *monobromide*, C_5NH_5,HBr,Br, which crystallises from alcohol and melts at 93°.

Pyridine methobromide dibromide, $C_5NH_5,MeBr,Br_2$, separates from alcohol in orange-red crystals, but is decomposed by acetone, and melts at 66°. *Pyridine ethobromide dibromide* is similar to the methyl compound and melts at 35°.

When chlorine is passed into aqueous pyridine hydrobromide, a somewhat unstable *substance* is formed which melts at 51° and probably has the composition $C_5NH_5,HCl,BrCl$. Pyridine methobromide, under the same conditions, yields a *dichloride*, $C_5NH_5,MeBr,Cl_2$, which is not stable, whilst from pyridine ethobromide, the *compound*, $C_5NH_5,EtBr,Cl_2$, is obtained.

On adding an excess of alcoholic iodine to pyridine hydrochloride, the chlorine is eliminated and the heptiodide,* C_5NH_5,HI,I_6 (this vol., i, 270), melting at 71—72°, is obtained; pyridine methochloride, under the same conditions, gives rise to pyridine methiodide tetriodide, whilst from pyridine ethochloride no definite compound could be prepared.

Pyridine hydrobromide dibromide, $C_5NH_5,HBr,Br_2 + 2H_2O$, formed on saturating with bromine a solution of pyridine in dilute hydrochloric acid, crystallises from alcohol in prisms and melts at 118—120°. On adding bromine to a chloroform solution of pyridine hydrochloride, the *perbromide*, C_5NH_5,HBr,Br, is formed; it crystallises in stellar aggregates of golden needles and melts at 88°. Pyridine methochloride yields with bromine a yellow *compound*, probably $C_5NH_5,MeBr,Br$, which melts at 82—83°, and a crystalline, orange-coloured *substance* melting at 55°, which is free from chlorine, and is probably the compound described by Ostermayer (Abstr., 1885, 813) as $C_5NH_5,MeBr,Br_2$, melting at 48°. When, however, pyridine methobromide is brominated, the *dibromide*, $C_5NH_5,MeBr,Br_2$, obtained melts at 66°. *Pyridine ethobromide dibromide*, $C_5NH_5\ EtBr,Br_2 + 2H_2O$, formed on passing bromine vapours through aqueous pyridine ethochloride, melts at 15°.

Chlorine does not produce perchlorides with either pyridine hydrochloride, methochloride, or ethochloride. W. A. D.

Euphthalmine. By CARL D. HARRIES (*Ber.*, 1898, 31, 665—666. Compare Abstr., 1897, i, 552).—Phenylglycolyl-N-methyl-β-vinyldiacetonalkamine has been found to be a powerful mydriatic, without affecting the accommodation, and has been termed *euphthalmine.* The *hydrochloride*, $C_{17}H_{25}O_3N,HCl$, is a stable, snow-white, crystalline product, which, after recrystallisation, loses the deliquescent character possessed by the crude material precipitated by hydrogen chloride from an ethereal solution of the base. It melts at 183—184°, and is very readily soluble in water. The *salicylate*, $C_{17}H_{25}O_3N,C_6H_4(OH)\cdot COOH$, melts at 115—116°. A. H.

γ-Halogen-derivatives of Piperidine. By HERMANN PAULY and CARL D. HARRIES (*Ber.*, 1898, 31, 666—668). γ-Iodo- and γ-bromopiperidine can be obtained by the action of the corresponding hydracids on vinyldiacetonalkamine. γ-Iodotrimethylpiperidine, $C_8H_{16}NI$, prepared by the action of hydriodic acid on either stereoisomeric form of vinyldiacetonalkamine, is identical with the product obtained by E. Fischer by the addition of hydrogen iodide to the corresponding acetonine.

* The melting point of this compound is given as 63—64° in the paper referred to.

γ-Bromotrimethylpiperidine, $NH<\begin{matrix}CHMe\cdot CH_2\\CMe_2-CH_2\end{matrix}>CHBr$, is a crystalline mass melting at 16°; its *hydrobromide*, $C_8H_{16}NBr,HBr$, is readily soluble in water and crystallises in pointed prisms, whilst the *picrate* forms brownish-yellow, quadratic tablets melting at 188—190°. The iodo-base reacts with silver mandelate to form *vinyldiacetonine mandelate* melting at 147°. A. H.

Action of Bromine on Triacetonamine. By HERMANN PAULY (*Ber.*, 1898, **31**, 668—674).—When aqueous triacetonamine is treated with a solution of bromine in aqueous potassium bromide, *N-bromotriacetonamine*, $CO<\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}>NBr$, is obtained as a pale yellow precipitate; it crystallises in long, ribbon-like forms melting at 44°, liberates iodine from potassium iodide, and does not form salts with acids. When the filtrate from this compound, or a solution of triacetonamine hydrobromide is treated in the same way with bromine, *perbromotriacetonamine hydrobromide*, $C_9H_{17}NO,HBr,Br_2$, is precipitated; this crystallises in golden yellow, flat needles, which decompose at 71—72°, and are so unstable that the compound could not be analysed. When the perbromide is heated at 80—90°, hydrogen bromide is evolved and *dibromotriacetonamine hydrobromide*, $C_9H_{15}NOBr_2$, HBr, formed, the same product being also obtained when bromine is added to a strongly acid solution of triacetonamine hydrobromide at 80—90°; it is sparingly soluble in most solvents, but crystallises from boiling hydrobromic acid in small, six-sided tablets, which decompose at 203°. The *free base* crystallises from benzene in slender needles, which have a satiny lustre and decompose at 140—150°. When either the free base or the hydrobromide is rapidly distilled with steam, an oil passes over which solidifies on standing, and then crystallises in pale emerald green prisms melting at 60—61°. This compound, which appears to be an isomeride of dibromotriacetonamine, dissolves in hydrobromic acid, forming a solution from which it is reprecipitated by sodium carbonate. When dibromotriacetonamine is heated with water for some time and then distilled in steam, the oil which passes over contains no bromine, boils at about 170°, and has an odour resembling that of menthol. Owing to the small quantity obtained, the further properties of this compound could not be examined. Dibromotriacetonamine reacts with silver benzoate to form *benzoyloxybromotriacetonamine*, $C_{16}H_{20}NO_3Br$, which crystallises in slender needles melting at 114°. *Imidotriacetonamine*, $C_9H_{16}N_2O$, is formed by the action of ammonia on dibromotriacetonamine-hydrobromide, and crystallises in slender prisms, melts at 180—181°, readily sublimes in needles, turns litmus paper blue, and is poisonous. The *hydriodide*, $C_9H_{16}N_2O,HI$, crystallises in needles and the *platinochloride*, which is readily soluble in water, forms orange-coloured prisms; the *hydrochloride* and *hydrobromide* are both very readily soluble in water. The exact constitutions of dibromotriacetonamine and the imido-base have not yet been ascertained. A. H.

Action of Phosphorus Pentachloride on 1-Alkylpyridones and 1-Alkylquinolones. By OTTO FISCHER (*Ber.*, 1898, **31**, 609—612. Compare Abstr., 1893, i, 282).—The alkylpyridones and

alkylquinolones are in many respects analogous to the aposafranones, but, as in the case of the last-mentioned compounds, it is doubtful whether they are ketones or anhydrides. The aposafranones, when treated with phosphorus pentachloride, yield dichlorides such as $N{<}{C_6H_4\cdot\atop C_6H_4Cl}{>}NPhCl$, in which the two chlorine atoms have different functions, and would appear from this reaction to be anhydrides of the type $O{<}{C_6H_3:N \atop NR-C_6H_4}$. The following experiments were undertaken to ascertain how pyridones and quinolones behave with the same reagent, and it has been found that they lose an alkyl chloride and simply yield an α-substituted pyridine or quinoline, so that no conclusion can be drawn as to their constitution.

α-Methylpyridone (Decker, Abstr., 1892, 729; 1893, i, 279), when treated with phosphorus pentachloride, forms methylic chloride and α-chloropyridine, identical with that described by von Pechmann and Baltzer (Abstr., 1892, 208). N-Methylquinolone and the corresponding ethyl derivative both yield α-chloroquinoline.

This reaction affords an excellent method of preparing the α-chloro-derivatives of pyridine and quinoline, since the corresponding pyridones and quinolones are easily accessible. A. H.

Influence of Constitution on the Formation of Ring Compounds. By MAX SCHOLTZ (*Ber.*, 1898, 31, 627—632. Compare this vol., i, 305).—The law previously formulated that ortho-xylylenic bromide reacts with ortho-substituted aromatic amines to form derivatives of xylylenediamine, but with all other amines to form derivatives of dihydroisoindole, has been confirmed by the examination of a number of different aromatic amines containing various groups in various positions to the ring.

Aniline reacts with ortho-xylylenic bromide dissolved in alcohol or chloroform, to produce phenyldihydroisoindole, which melts when pure at 170—171° instead of 165° as previously stated. According to Leser (Abstr., 1884, 1313), the product consists of diphenylortho-xylylenediamine, melting at 172°, but a repetition of his experiment shows that the compound obtained by him was in reality the indole derivative. *Metabromophenyldihydroisoindole*, $C_6H_4{<}{CH_2 \atop CH_2}{>}N\cdot C_6H_4Br$, crystallises in colourless needles melting at 112°, whilst the *parabromo*-compound also forms needles and melts at 184°. *Metachlorophenyldihydroisoindole* crystallises in arborescent groups of needles melting at 101°, whilst the *parachloro*-compound crystallises in plates and melts at 170°. *Metanitrophenyldihydroisoindole* crystallises in orange-red, lustrous needles melting at 177°, whilst the *paranitro*-derivative crystallises in yellow needles. Orthonitraniline, on the other hand, yields *diorthonitrophenylxylylenediamine*, $C_6H_4(CH_2\cdot NH\cdot C_6H_4\cdot NO_2)_2$, which crystallises in yellow needles melting at 211—212°.

Orthamidobenzoic acid reacts like other ortho-substituted amines, and yields *xylylenebisamidobenzoic acid*, $C_6H_4(CH_2\cdot NH\cdot C_6H_4\cdot COOH)_2$, which is sparingly soluble in hot water and melts at 259—260°. The *barium* and *calcium* salts are soluble in hot water. With xylylenic

bromide, metamidobenzoic acid yields *dihydroisoindolebenzoic acid*, $C_6H_4<\substack{CH_2\\CH_2}>N\cdot C_6H_4\cdot COOH$, which crystallises in colourless needles melting at 246—247°. The *potassium*, *sodium*, and *ammonium* salts are but sparingly soluble in water. A. H.

The Base Prepared by E. Fischer from Methylketol and Methylic Iodide. By KARL BRUNNER (*Ber.*, 1898, **31**, 612—615).—The base, $C_{12}H_{15}N$, obtained by Fischer and Steche (Abstr., 1888, 298) by the action of methylic iodide on methylketol, has been hitherto regarded as trimethyldihydroquinoline, but it does not yield quinoline derivatives on oxidation, indolinone being produced (Ciamician, Abstr., 1897, i, 101).

This base is formed when methylisopropylmethylphenylhydrazone is treated with alcoholic zinc chloride; the hydriodide, therefore, has the constitution $C_6H_4<\substack{CMe_2\\NMeI}>CMe$, whilst the free base is either $C_6H_4<\substack{CMe_2\\NMe}>CMe$ or $C_6H_4<\substack{CMe_2\\NMe}>C{:}CH_2$. A. H.

Heumann's Synthesis of Indigo. By W. HENTSCHEL (*J. pr. chem.*, 1898, **57**, 198—201).—In repeating Heumann's process for the production of indigo, namely, fusing phenylglycine with potash, the author finds that the yield is only from 8·6—11·5 per cent. of the theoretical, and the major portion of the phenylglycine can be recovered unchanged. If the residue, after precipitating the colouring matter, is remelted with potash, a further quantity of indigo is obtained.

Attempts to improve the process have so far proved unsuccessful, but the author proposes to further investigate the matter. A. W. C.

Glauconic Acids, a New Group of Quinoline Dyes. By OSCAR G. DOEBNER (*Ber.*, 1898, **31**, 686—696).—The name glauconic acids is given to a series of dyes obtained by the action of aniline or para-alkyl derivatives of aniline on pyruvic acid and formaldehyde. Their salts are bluish-violet dyes, and, like the cyanines and quinoline red, are not at all fast as regards light and acids. *Hydroglauconic acid* $CH\left(C_6H_3<\substack{NH\text{———}CHMe\\C(COOH){:}CH}\right)_3$, is prepared by gradually adding pyruvic acid (100 grams) to a warm solution of aniline (50 grams) in absolute alcohol (150 grams) contained in a dish on a water bath; at the end of 15 minutes, the evolution of carbonic anhydride ceases and 40 per cent. formaldehyde (50 grams) is gradually run in; the colour then changes to brown, and carbonic anhydride is again evolved. The mixture is now heated for an hour on the water bath, fresh alcohol being added if necessary, and after remaining for 6 hours, the cold mixture is treated with a small quantity of alcohol and then a large quantity of acetone added, when the hydroglauconic acid is thrown down in the form of yellow aggregates. After being rubbed in a mortar with ether and well washed with the same solvent, it may be recrystallised from hot methylic alcohol. It melts and decomposes at about 192°, is sparingly soluble in water, acetone or ether, but dissolves more readily

in hot methylic or ethylic alcohol, is soluble in both hydrochloric and acetic acids, and is thrown down unaltered on the addition of water; it also dissolves to some extent in cold alkali, but on warming, the blue alkali salts of glauconic acid are obtained. If pyruvic acid is used in the proportion of 1 mol. instead of 2 mol. to every molecule of aniline, a sparingly soluble *anilide* of hydroglauconic acid is obtained. When subjected to dry distillation, the hydro-acid is mainly converted into carbonic anhydride and *dihydroquinaldine*, which boils at 245—247°; this compound can, however, be more readily obtained by heating quinaldine hydrochloride with zinc dust; it yields a *picrate* melting at 187° and a *platinochloride* crystallising in red needles.

Hydroglauconic acid can readily be oxidised to *glauconic acid* either by warming with alkalis alone, or in the presence of air, or by the aid of bromine water or of formaldehyde.

The method recommended is to heat the hydro-acid (10 grams) with alcohol (10 grams) in a dish, then to add 10 per cent. sodium hydroxide (100 c.c.), and when the mixture begins to boil to add 40 per cent. formaldehyde (15 c.c.), and to continue the boiling for a minute. On the addition of an excess of alcohol, *sodium* glauconate, $C_{34}H_{28}N_3O_6Na$, separates in the form of blue needles. The acid itself, $\left.\begin{array}{l} CH\cdot CHMe\cdot N— \\ C(COOH)—C_6H_3 \end{array}\right\rangle C\left(C_6H_3\left\langle\begin{array}{l} NH——CHMe \\ C(COOH):CH \end{array}\right.\right)_2$, crystallises in dark blue needles, is insoluble in water, alcohol, or ether, but dissolves in glacial acetic acid, yielding a blue solution; this blue colour changes to pink and finally disappears on the addition of zinc dust. When subjected to dry distillation, it yields dihydroquinaldine. The *sodium* salt is sparingly soluble in cold water, but dissolves in hot water, yielding a bluish-purple solution; the *calcium*, *barium*, and *aluminium* salts are obtained in the form of blue precipitates. *Hydroparethoxyglauconic acid*, obtained from paraphenetidine, pyruvic acid, and formaldehyde, is a yellow powder melting and decomposing at about 190°; it is insoluble in water, but dissolves in alcohol or acetone. *Parethoxyglauconic acid*, $C_{40}H_{41}N_3O_9$, crystallises in dark blue needles, insoluble in alcohol but soluble in acetic acid. Its *sodium* salt, $C_{40}H_{40}N_3O_9Na$, crystallises from hot water in glistening plates, and yields a blue solution with a red fluorescence.

Hydro-β-naphthaglauconic acid, $C_{46}H_{37}N_3O_6 + 5H_2O$, obtained from β-naphthylamine, pyruvic acid, and formaldehyde, crystallises from hot methylic alcohol in large, colourless, prismatic crystals. It loses its water at 110°, and decomposes at 231° into carbonic anhydride and dihydronaphthaquinaldine. The acid is insoluble in ether, acetone or water, but dissolves in hot methylic or ethylic alcohol as well as in dilute alkalis. *Dihydronaphthaquinaldine*, $C_{10}H_6\left\langle\begin{array}{l} NH\cdot CHMe \\ CH:CH \end{array}\right.$, is a thick, yellow oil distilling somewhere above 300°; it yields a sparingly soluble *picrate* and *platinochloride*. The yield of *β-naphthaglauconic acid*, $C_{46}H_{35}N_3O_6 + \frac{1}{2}H_2O$, obtained from the hydro-acid, is very poor (about 15 per cent.). It is deposited in the form of blue, curved needles when its alkali salts are dissolved in concentrated hydrochloric acid and then poured into water; it is insoluble in water,

alcohol, or ether, but dissolves in acetic acid, giving a blue solution. Its *sodium* salt, $C_{46}H_{34}N_3O_6Na + 8H_2O$, and *potassium* salt with $8H_2O$, are soluble in hot water, and give pure blue solutions. J. J. S.

Oxidation of Hydrazoximes. By GIACOMO PONZIO (*J. pr. chem.*, 1898, **57**, 160—172).—*Phenyl*-2 : 3-*Dimethyl*-1 : 2-*oxy-pyrro*-1 : 4-*diazole* is obtained by the action of nitric peroxide or mercuric oxide on diacetylhydrazoxime, when oxidation takes place with elimination of two hydrogen atoms, this reaction appearing to be a general one for all hydrazoximes. It crystallises from light petroleum in prisms, often several centimetres long, melting at 92—93°, and cannot be distilled at ordinary atmospheric pressure without decomposition. A determination of the molecular weight by Beckmann's method gave 185·1 (calculated 189). It is a very feeble monacid base, forming a *hydrochloride* melting and decomposing at 120°. It does not react with phenylhydrazine, acetic anhydride, or methylic iodide, but when treated with hydriodic acid or nascent hydrogen is reduced to phenyldimethylosotriazole, for which reason, and also its behaviour towards halogen acids, the author ascribes to it the following formula, $O\Big\langle\begin{matrix} CMe\text{—}CMe. \\ | \qquad\quad \| \\ N\cdot NPh\cdot N \end{matrix}$

Nitrophenyldimethylosotriazole, $C_2N_3Me_2\cdot C_6H_4\cdot NO_2$, obtained by the action of nitric acid on phenyldimethylosotriazole, crystallises from alcohol in yellow needles melting at 227° and is almost insoluble in the ordinary organic solvents. When suspended in alcohol and reduced with zinc and hydrochloric acid, the corresponding *amido*-derivative is produced, forming small, faintly-coloured prisms melting at 123—124°; its *hydrochloride* is a white, insoluble substance decomposing at 240°, and the *acetyl* derivative forms beautiful needles melting at 139°.

When phenyldimethyloxypyrrodiazole is treated with bromine water, a *bromo*-derivative, $C_{10}H_{10}N_3BrO$, is obtained, which crystallises from alcohol in beautiful yellow needles melting at 109—110°. It is reduced in alcoholic solution to *bromophenyldimethylosotriazole*, $C_{10}H_{10}N_3Br$, which is also produced by the action of bromine water on the triazole; this crystallises in white needles and melts at 152—153°. *Phenyldimethyloxypyrrodiazolecarboxylic acid*, $C_2N_3OMePh\cdot COOH$, obtained by the action of potassium permanganate on the free base, crystallises from light petroleum in very slender, white needles melting at 93°; it is only slightly soluble in water, but readily in ether, chloroform, and acetone.

When phenyldimethyloxypyrrodiazole is heated in sealed tubes with hydrochloric acid for 3 hours at 150°, there is produced, besides phenyldimethylosotriazole, a *chloro*-compound, $C_2N_3HMe_2PhCl$, crystallising from ether in white prisms melting at 152° and boiling at 285°; it has no basic properties, and does not react with acetic or benzoic chlorides, acetic anhydride, or nitrous acid, but with nitric acid it yields a *mononitro*-derivative crystallising in long, glistening, yellow needles melting at 116°. On further heating with nitric acid in sealed tubes, it loses the elements of hydrogen chloride, forming mononitrophenyldimethylosotriazole, and when oxidised with chromic acid it yields a *carboxylic acid*, $C_2N_3HMePhCl\cdot COOH$, crystallising in colourless prisms and melting and decomposing at 240—242°.

The corresponding *bromo*-compound, $C_2N_3HMe_2PhBr$, forms colourless prisms melting at 150—151°, and the *iodo*-compound colourless prisms melting at 142°. A. W. C.

Isocreatinine, a Compound obtained from the Flesh of the Haddock. By JÖRGEN E. THESEN (*Zeit. physiol. Chem.*, 1897, **24**, 1—17).—On digesting the muscular tissue of the haddock (*Gadus Morrhua*) twice with a large quantity of water at 40°, and subsequently evaporating the extract, the albumin coagulates and is removed, whilst the inorganic salts are precipitated by adding alcohol; the filtrate from these is then evaporated to a thick syrup, which is repeatedly boiled with alcohol. The solution obtained deposits yellow, microscopic needles of *isocreatinine*, which, on recrystallisation from 50 per cent. alcohol, separates in beautiful, lustrous leaflets which, when heated to 230—240°, decompose without melting. Its analysis, and a determination of the molecular weight by the cryoscopic method, point to the formula $C_4H_7N_3O$; the base is thus isomeric with creatinine. The *hydrochloride*, $C_4H_7N_3O,HCl$, crystallises from alcohol in dull-yellow needles, whilst the *sulphate* separates from water on adding alcohol and ether in brittle, transparent, yellow plates; the *oxalate*, $C_4H_7N_3O,C_2H_2O_4$, crystallises from alcohol in long, slender, light-golden needles. Isocreatinine unites with cadmium chloride to form the *double salt*, $C_4H_7N_3O,CdCl_2$, which separates from water in slender needles; the *zinc* double salt, $C_4H_7N_3O,ZnCl_2$, crystallises from water on the addition of alcohol, whilst the *platinochloride*,

$$C_4H_7N_3O,H_2PtCl_6 + 2H_2O,$$

crystallises from dilute alcohol in red needles which lose their water at 110° and become yellow.

An alkaline solution of copper sulphate produces a blue coloration with isocreatinine, and on heating to 80°, a precipitate of cuprous and cupric oxides is formed; in presence of a reducing agent, copper sulphate produces a bright green precipitate which becomes brownish-black on heating. Isocreatinine is not precipitated by potassium mercuric iodide, potassium cadmium iodide, silver nitrate, lead acetate, copper acetate, or tannic or picric acid; and does not give the murexide or biuret reactions. Like creatinine, however, it produces a red coloration with a solution of picric acid to which a few drops of caustic soda have been added (Jaffé's reaction); and with sodium nitroprusside and caustic soda, a red coloration is produced (Weyl's reaction), which changes to blue on adding acetic acid and warming (Salkowski's reaction).

When left in contact with milk of lime, isocreatinine appears to be converted into creatine; on oxidation with 0·5 per cent. potassium permanganate, potassium oxalate is formed, but no methylguanidine. On being heated with barium hydroxide, ammonia is evolved, but no definite product could be isolated. When isocreatinine is heated for several hours with concentrated sulphuric acid containing 10 per cent. of phosphoric anhydride, no decomposition takes place, the sulphate alone being formed.

Isocreatinine differs from ordinary creatinine and from the modifications "natural" and "tabular" creatinine present in urine (Johnson,

Abstr., 1889, 165), in colour, in cupric-reducing power, and in its solubility, and that of its platinochloride and picrate, in alcohol and water; isocreatinine yields, with potassium permanganate, ammonia, but no methylguanidine, whilst creatinine gives rise to the latter, but no ammonia. W. A. D.

Hydrocinchonine. By OSWALD HESSE (*Annalen*, 1898, **300**, 42—59).—Hydrocinchonine, $C_{19}H_{24}N_2O$, was first obtained by Caventou and Willm on oxidising commercial cinchonine sulphate with potassium permanganate, the substance being an impurity of the crude alkaloid; Skraup has referred to this substance as cinchotine, but the author prefers to use the name employed by its discoverers. The proportion of hydrocinchonine occurring in cinchona bark is small, the most profitable source of the base being the bark of *Remijia Purdieana*, in which it is also found associated with cinchonine; the hydro-base is separated by means of its platinochloride.

Hydrocinchonine melts at 268—269°. A 0·6 per cent. solution in absolute alcohol has the specific rotatory power $[\alpha]_D = 204·5°$, whilst a 5 per cent. solution in a mixture of chloroform and absolute alcohol (2 : 1) has the specific rotatory power $[\alpha]_D = 188·2°$; an aqueous 5 per cent. solution of the sulphate has the specific rotatory power $[\alpha]_D = 224·2°$. The *normal platinochloride*, $(C_{19}H_{24}N_2O)_2,H_2PtCl_6$, forms a yellow, flocculent precipitate, which soon changes into orange needles; it is anhydrous, and dissolves with difficulty in water. The *acid platinochloride*, $C_{19}H_{24}N_2O,H_2PtCl_6$, is obtained as a yellow, flocculent precipitate, which undergoes no change in contact with the mother liquor; it contains $2H_2O$, and when prepared in an acid solution, separates in long prisms containing $4H_2O$.

The sulphate occurs in four modifications, differing from one another in the amount of water of crystallisation which they contain. The form which has been already described contains $12H_2O$, and crystallises in long, lustrous needles; a second modification crystallises in leaflets which gradually change into tetragonal double pyramids and contain $9H_2O$. The sulphate also crystallises in forms containing $6H_2O$ and $2H_2O$. A 5 per cent. solution of the dried salt in chloroform has the specific rotatory power $[\alpha]_D = 138·0°$, a solution of the same concentration in absolute alcohol giving $[\alpha]_D = 160·8°$.

Acetylhydrocinchonine is amorphous, and is precipitated from solutions in dilute acids by ammonia; the alcoholic solution is strongly alkaline. A 3 per cent. solution in absolute alcohol has the specific rotatory power $[\alpha]_D = 105·7°$. The *hydrochloride* crystallises in colourless needles, and dissolves very readily in water. The *platinochloride* separates as a yellow, flocculent precipitate containing $1H_2O$; when gently heated with dilute hydrochloric acid, this form changes into small, orange-red needles containing $2H_2O$.

Hydrocinchoninesulphonic acid, $C_{19}H_{23}N_2O·SO_3H$, is prepared by dissolving the dehydrated sulphate in concentrated sulphuric acid (sp. gr. = 1·84), and after an interval of 24 hours, pouring the liquid into cold water (compare Skraup, this vol., i, 51); it crystallises from hot water and from 50 per cent. alcohol in colourless needles containing $1H_2O$. The sulphonic acid dissolves in 714 parts of water at

15°, the solution having an acid reaction; the substance becomes anhydrous at 110°, and melts at 224°. The *hydrochloride* crystallises in colourless, lustrous needles, and contains $5H_2O$; the *platinochloride* forms short, orange prisms containing $6H_2O$. The *sulphate* separates in white, lustrous needles with $8H_2O$; an aqueous 3 per cent.. solution of the hydrated salt has the specific rotatory power $[\alpha]_D = 166°$ Hydrocinchoninesulphonic acid undergoes partial hydrolysis when heated with ammonia. M. O. F.

Pilocarpidine. By JOSEF HERZIG and HANS MEYER (*Monatsh.*, 1898, **19**, 56—59).—When pilocarpine hydrochloride is fused, it is converted without loss in weight into pilocarpidine hydrochloride which is shown by the authors to contain a methyl group attached to nitrogen, whereas Merck's pilocarpidine does not. Moreover, the aurochloride of the latter melts at 120—124°, and that of the pilocarpidine obtained by fusing pilocarpine hydrochloride at 153—156°. It is therefore to be concluded that several so-called pilocarpidines exist. A. W. C.

Action of Reducing Agents on Cholic Acid. By MICHAEL SEŃKOWSKI (*Monatsh.*, 1898, **19**, 1—4).—In earlier researches on the reduction of cholic acid, deoxycholic acid was obtained by Mylius by the putrefaction of bile or salts of cholic acid, and by Vahlen by the action of zinc dust in acetic acid solution on cholic acid (Abstr., 1897, i, 647); the author has now attempted to throw light on the constitution of cholic acid by subjecting it to the action of more energetic reducing agents.

When cholic acid is treated with hydriodic acid in presence of amorphous phosphorus, there is obtained a yellowish, brittle, resinous mass which is apparently *cholylic anhydride*, $(C_{24}H_{39}O)_2O$. It melts at 75—80°, but could not be obtained crystalline. Dilute potash dissolves it, forming an opalescent alkaline solution, from which concentrated potash precipitates the *potassium* salt of cholylic acid, characterised, as are also the *barium, lead, copper, silver, zinc* and *calcium* salts by not possessing a bitter taste. Cholylic acid seems not to be obtainable in the free state.

When the anhydride is dissolved in alcohol and the solution saturated with hydrogen chloride, a sticky, reddish-brown mass is produced probably consisting for the most part of *ethylic cholylate*, but neither this substance nor the *nitrile*, obtained by the action of lead thiocyanate on the anhydride, could be procured in a state fit for analysis. *Bromo-* and *nitro-*substitution products of the anhydride have been obtained, and will be dealt with more fully in a future communication. A. W. C.

Urobilin. By F. GOWLAND HOPKINS and ARCHIBALD E. GARROD (*J. Physiol.*, 1898, **22**, 451—464. Compare Abstr., 1896, i, 712).—Maly's hydrobilirubin is not the same substance as urobilin, but by allowing the action of sodium amalgam on bilirubin to proceed beyond the stage indicated by Maly, a product is obtained which resembles natural urobilin very closely in its spectroscopic appearance; the E band, however, was never obtained.

In elementary composition, urinary and fæcal urobilin are identical

(C, 63·58; H, 7·84; N, 4·11 per cent.). The percentage of nitrogen in hydrobilirubin is 9·57 (Maly gives 9·22). W. D. H.

Egg-albumin. By KARL DIETERICH (*Chem. Centr.*, 1897, ii, 422—423; from *Pharm. Centr.-H.*, **38**, 449—453).—Fresh white of egg loses 87—88 per cent. of its weight when dried at 100° and for the preparation of a kilogram of "*albumen ovi siccum*" containing about 16—17 per cent. of water, 7—8 kilograms of the white of egg are necessary. Fresh white of egg also contains some yolk and about 1 per cent of fibrin, &c.; the latter can be removed by beating and filtering through cloth. The iodine absorption number of fresh white of egg is about 155 and that of fibrin 174—178. White of egg which contains fibrin partly dissolves in water, although with difficulty, forming a turbid solution and the residual insoluble portion (6·32 per cent. in one case) is greater than that obtained from white of egg free from fibrin (3·97 per cent.); the soluble portion of the latter, moreover, dissolves more quickly and forms a clear solution. White of egg which contains no fibrin is easily soluble in dilute (30 per cent.) acetic acid, giving a solution which remains clear on adding water or alcohol. Fibrin is insoluble in acetic acid, and hence white of egg which contains fibrin, only partially dissolves and when water or alcohol is added to the solution only the very small quantity of dissolved fibrin is precipitated. *Albumen ovi siccum* forms a transparent, horny mass, or a yellowish, tasteless, odourless powder, is insoluble in alcohol, and gives a neutral, turbid solution in water. When 5 c.c. of the aqueous solution (1/1000) is carefully warmed with 10 drops of nitric acid, there is an abundant separation of coagulated albumin. The amount of iodine absorbed by this substance should be at least 12 per cent., and the content of water 16—17 per cent. (dried at 100°). The portion insoluble in water should not amount to more than 4—5 per cent. 0·1 gram of the powder when boiled with 10 c.c. of 30 per cent. acetic acid should dissolve completely in 5 minutes, and the solution should not give a precipitate on adding 20 c.c. of water or alcohol. E. W. W.

Iodalbumin. By FRANZ HOFMEISTER (*Zeit. physiol. Chem.*, 1897, **24**, 159—172).—When purified crystallised egg-albumin (20 grams) is heated during 4 hours with a mixture of potassium iodide (10 grams), potassium iodate (5 grams) and concentrated sulphuric acid (4 c.c.) dissolved in 400 c.c. of water, *iodalbumin* is precipitated as a light-brown powder which is insoluble in water; it dissolves in alkalis, but separates as a white, gelatinous precipitate on adding dilute acids, although soluble in excess. Iodalbumin, after being carefully purified by successive precipitations, contains 8·95 per cent. of iodine, none of which is removed by continued washing with water or aqueous potassium iodide. It resembles albumin in being precipitated by potassium ferrocyanide, and in giving the xanthoprotein and biuret reactions, and the sugar reaction in presence of α-naphthol (Molisch); it fails, however, to give Millon's or Adamkiewicz's reactions, and does not produce lead sulphide when boiled with alkaline lead oxide. From the latter fact, the author concludes that the sulphur exists in an oxidised (sulphonic) form in iodalbumin, and partially in the form of a mercaptan or sulphide in ordinary albumin.

On the ground of previous analyses, the author attributes to crystallised egg-albumin the composition $C_{239}H_{386}N_{58}S_2O_{78}$, whilst to iodalbumin, the formula $C_{227}H_{370}I_4N_{58}S_2O_{75}$ is given. Its formation is explained by assuming that 4 atoms of hydrogen in albumin are displaced by iodine, whilst 3 atoms of oxygen are added in the oxidation of 1 atom of sulphur; 2 mols. of a carbohydrate, $C_6H_{12}O_6$, are eliminated from, and 6 mols. H_2O added to, the molecule of albumin. This view is supported by the fact that a considerable proportion of a carbohydrate yielding a crystalline osazone was formed in the preparation of iodalbumin, owing to the hydrolytic action of the sulphuric acid employed.

When iodalbumin is digested with pepsin, peptone is formed and iodine liberated; when administered to rabbits, alkaline iodides are found in the urine after a few hours, but no toxic effects are produced.

W. A. D.

[NOTE BY ABSTRACTOR.—A product, probably identical with iodalbumin and possessing all the properties of the latter, was prepared by Hopkins (this vol., i, 54 and 99) from a solution of egg-albumin; it contained, however, only 6·28 per cent. of iodine.]

Proteids of the Maize Kernel. By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1897, **19**, 525—532. Compare Chittenden and Osborne, Abstr., 1892, 379, 746 and 749).—By precipitating an aqueous extract of maize meal with ammonium sulphate and dissolving the precipitate in water, a solution is obtained from which the globulins can be completely removed by dialysing and subsequently heating to 80°; if alcohol is then added, a small quantity of a *proteid* is precipitated which shows many of the reactions of the proteoses. It appears that whilst no true albumin is present in maize, three globulins can be separated; the first of these, *maysin*, formerly called "maize myosin," is completely extracted from the meal by water alone; its solution in 10 per cent. brine coagulates at 70°, whilst that of *maize globulin*, the "albumin" of the previous paper, coagulates at 62°. *Maize edestin* is much less soluble in saline solutions than either of the foregoing; its solution in 10 per cent. brine is only partially coagulated by boiling.

Zein, extracted from maize meal by hot 85—95 per cent. alcohol, is insoluble in water and in absolute alcohol, but is easily soluble in glycerol heated to 150°, and remains unchanged when the latter solution is heated to 200°; it dissolves without change in warm phenol and in boiling glacial acetic acid, but is insoluble in 0·5 per cent. sodium carbonate, and in 0·2 per cent. hydrochloric acid; in 0·1—2·0 per cent. caustic potash it dissolves easily, but is not converted into alkali albumin, even after heating at 40° during 24 hours. Alcoholic solutions of zein are not precipitated by tannin, picric acid, trichloracetic acid, lead acetate, silver nitrate, mercuric chloride, ferric chloride, or potassio-mercuric iodide. The clear films produced by evaporating on glass an alcoholic solution of zein to which silver nitrate has been added, gradually turn deep red on exposure to sunlight.

In addition to the proteids described, a 0·2 per cent. solution of potash dissolves a substance which is insoluble in salt solutions and alcohol, and contains 2·38 per cent. of ash.

The following table gives analyses of the proteids present in maize meal, as well as the proportions in which they occur.

Proteid.	Percentage of maize.	Composition.				
		C.	H.	N.	S.	O.
Proteose	0·06	—	—	17·00	—	—
Maysin	0·25	52·68	7·02	16·76	1·30	22·24
Maize globulin	0·04	52·38	6·82	15·25	1·26	24·29
Maize edestin	0·10	51·43	6·86	18·06	0·86	22·79
Zein	5·00	55·23	7·26	16·13	0·60	20·78
Proteid soluble in 0·2 per cent. potash	3·15	51·26	6·72	15·82	0·90	25·30

W. A. D.

Decomposition of Casein by Hydrochloric Acid. By THEODOR PANZER (*Zeit. physiol. Chem.*, 1897, **24**, 138—141).—Purified casein was heated during 5 hours with concentrated hydrochloric acid (sp. gr. = 1·19), and during several days with its 20 per cent. solution; large quantities of glutamic acid, which was characterised by analysis and crystallographic measurement, were obtained; the statement of Cohn (Abstr., 1896, i, 658) that the latter is only formed in small quantity under the above conditions is, therefore, incorrect.

W. A. D.

Organic Chemistry.

Chemical Effects of the Silent Electric Discharge. By MARCELLIN E. BERTHELOT (*Compt. rend.*, 1898, **126**, 561—567, 567—575, 609—616, 616—627).—The author has made a new series of experiments on the chemical effects of the silent electrical discharge, with particular reference to the combination of nitrogen with various carbon compounds. The compound or mixture under examination was enclosed in a narrow space (about 1 mm. across), through which passed the discharge from a coil fitted with a Marcel-Deprez contact-breaker, and connected with a Leyden jar. The spark from the coil under these conditions was 12 to 15 mm. in length; the discharges were alternating. As a rule, the discharge was allowed to act for 24 hours. Liquids with a high vapour tension behaved very much like gases, whereas in the case of liquids such as oil, with a very low vapour tension, it was almost impossible to reach the limit of the reaction. In many cases, the intermediate products were examined, and were usually found to differ materially from the final products. The relative velocities of the primary and secondary reactions play an important part in determining the final result. The velocity and nature of the reactions seem to be functions of the intensity of the discharge. Under all circumstances, it is important to avoid any actual sparking. As a rule, the final equilibrium is dependent on the formation of solid or resinous products which have a low vapour tension and a low electric conductivity.

When absorption of nitrogen takes place, the product is of the nature of an amine or an amido-derivative, and frequently seems to be a poly-amine; azo-, nitroso-, and nitro-derivatives, hydrazines, hydrogen cyanide, or ammonium cyanide are not formed.

Several hydrocarbons were examined, both alone and when mixed with an equal volume of nitrogen. Methane loses about half its hydrogen, and yields a solid product, $C_{10}H_{18}$; a small quantity of acetylene is formed in the early stages of the decomposition, but afterwards disappears. In presence of nitrogen, the methane loses about half its hydrogen, and the nitrogen absorbed is rather less than one-fourth of the volume of hydrogen liberated; the solid product, which has the empirical composition C_2H_3N, and is probably a tetramine of the nature of a polymerised acetylenamine, is alkaline to litmus.

Ethane loses about one-third of its hydrogen, and the condensation product, $C_{10}H_{18}$, has practically the same composition as the product from methane, but is not identical with it. In presence of nitrogen, the solid product, $C_{16}H_{32}N_4$, is similar to that obtained from methane, except that the ratio of carbon to nitrogen in the product from ethane is twice as high as in the product from methane. Ethylene is rapidly condensed to a liquid under the influence of the discharge, whilst small quantities of acetylene and ethane are formed; the latter eventually disappear, and the solid product has the composition C_8H_{14}. In presence of nitrogen, the product is an alkaline solid of

the composition $C_{16}H_{32}N_4$, the volume of nitrogen absorbed being practically equal to the volume of hydrogen liberated.

Acetylene yields first a liquid, and afterwards a solid, which decomposes explosively when heated, and is rapidly oxidised when exposed to air. In presence of nitrogen, the phenomena are at first the same as with acetylene alone, but after a time the nitrogen is absorbed, with formation of a solid product, $C_{16}H_{16}N_2$. No hydrogen is liberated.

Propylene at first condenses rapidly to a liquid, and afterwards a solid is formed of the composition $C_{15}H_{26}$, some hydrogen being liberated. With nitrogen, the phenomena are similar, but gradually nitrogen is absorbed and hydrogen is liberated, the product, $C_{15}H_{28}N_4$, being a whitish resin with an alkaline reaction, the volume of nitrogen absorbed being practically double that of the hydrogen liberated.

Trimethylene, when alone, behaves in the same way as propylene, and yields practically the same product; but in presence of nitrogen, the product, although similar to that from propylene, contains less hydrogen, the volume of hydrogen liberated being practically equal to the volume of nitrogen absorbed.

Allylene rapidly condenses to a solid with a pungent empyreumatic odour, a small quantity of hydrogen being liberated in presence of nitrogen. No hydrogen is liberated, but the nitrogen is absorbed, and the product has the composition $C_{15}H_{20}N_2$.

Carbonic oxide is converted by the discharge into carbonic anhydride and the suboxide, C_4O_3, as the author and Brodie showed many years ago; the suboxide is a brown solid which dissolves in water, and forms an acid solution. In presence of nitrogen, the results are the same as with carbonic oxide alone. In presence of excess of hydrogen, the two gases condense in practically equal volumes, without formation of either carbonic anhydride or acetylene. The product $(CH_2O)_n$ is a mixture of polymerides of formaldehyde, some being soluble and others insoluble in water; they have no reducing action on Fehling's solution. When the carbonic oxide is in excess and not the hydrogen, the product has the empirical composition $C_3H_4O_3$, and its aqueous solution has some reducing power. With carbonic oxide, nitrogen, and hydrogen, the product $(CH_3NO)_n$ may be regarded as a condensed formamide. When the hydrogen in the gaseous mixture is not in excess, the product is a mixture of substances which dissolve in water and yield ammonia when boiled with an alkali, and substances which are insoluble in water and seem to be related to the quinolines. The complex nitrogen derivatives may be regarded as formed by the substitution of nitrogen in the carbohydrate formed by the action of the discharge on the carbonic oxide and nitrogen.

Carbonic anhydride alone yields percarbonic anhydride and the suboxide previously described. With a mixture of carbonic anhydride with twice its volume of hydrogen, the product is a carbohydrate identical with that formed by carbonic oxide under similar conditions. If the anhydride is mixed with an equal volume of nitrogen and three times its volume of hydrogen, the residual gas contains no carbon, but consists of equal volumes of nitrogen and hydrogen; the solid product, when heated with water, yields an effervescing solution containing ammonium nitrite. It may be regarded as a mixture of ammonium

nitrite with the amido-compound formed by carbonic oxide; possibly it may be a true azo-compound dissociable by water. With 4 vols. of hydrogen instead of 6, more of the nitrogen is left.

The action of the silent discharge on carbonic oxide or carbonic anhydride in presence of hydrogen and nitrogen may be compared with the interactions of water and carbonic anhydride in plants, or with the action of heat on salts of formic acid. The general results confirm the author's earlier views as to the great importance of the CH_2O group and its reactions.

In the experiments with alcohols, the reaction was, as a rule, carried to its limit wherever possible.

With methylic alcohol and nitrogen, the latter is absorbed and an equal volume of hydrogen is liberated, together with a small quantity of carbonic oxide; the solid product contains $C_4H_{12}N_2O_4$, and is probably one of the complex amidines or their hydrates. At the beginning of the reaction, some hydrogen, methane, carbonic oxide, and carbonic anhydride are formed, and at a later stage the proportion of methane is still higher, but eventually it disappears, together with the carbonic anhydride.

Ethylic alcohol in presence of nitrogen yields hydrogen, traces of carbonic anhydride, and a solid product, $C_{10}H_{20}N_4O_5$; the hydrogen liberated per molecule of ethylic alcohol is double that liberated per molecule of methylic alcohol, and the same ratio holds good for the quantity of nitrogen absorbed. In the early stages of the reaction, ethane and carbonic oxide are formed, but subsequently disappear.

Propylic and isopropylic alcohols behave in much the same way as ethylic alcohol. Nitrogen is absorbed, and twice as much hydrogen is liberated; the solid product is $C_6H_{12}N_2O_2$.

Allylic alcohol yields a strongly alkaline solid product, the empirical formula of which is $C_9H_{16}N_2O_3$. The quantity of hydrogen liberated is very small, and is equal to about one-third of the volume of nitrogen absorbed.

Phenol, under similar conditions, absorbs nitrogen, but no other gas is liberated, and the solid remains neutral. In the case of dihydric phenols, very little nitrogen is absorbed by the meta- and para-derivatives, but the ortho-derivative absorbs a considerable quantity, and yields a neutral product. Pyrogallol absorbs a small quantity of nitrogen, and gives off small quantities of hydrogen and carbonic oxide.

Glycollic ether, with an equal volume of nitrogen, yields small quantities of ethane and hydrogen, but no carbon oxides. A volume of nitrogen equal to the volume of the glycollic ether is absorbed, and the solid product contains $(C_2H_4N_2O)_n$. It is an isomeride of cyanamide hydrate.

Methylic ether, with excess of nitrogen, yields the substance $C_2H_{4\cdot3}ON_{1\cdot25}$, the ratios approximating closely to those of the compound obtained from ethylic alcohol; hydrogen is liberated in quantity larger than the nitrogen absorbed, but neither carbon oxides nor acetylene is formed.

Ether, with excess of nitrogen, yields a substance, $C_4H_{6\cdot4}N_2O$, the hydrogen liberated having about double the volume of the nitrogen

absorbed, whilst the latter is practically equal to the volume of the ether in the form of gas.

Most of the products formed in presence of nitrogen are probably closed chain compounds belonging to the pyridine and quinoline groups.

C. H. B.

Formation of Mixed Hydrates of Acetylene and of other Gases. By ROBERT DE FORCRAND and SULLY THOMAS (*Compt. rend.*, 1897, **125**, 109—111).—A crystalline mixed hydrate is obtained when pure acetylene gas saturated with carbon tetrachloride vapour is passed into a flask containing small pieces of ice, and kept at 0°. The pressure in the flask is kept at about $1\frac{1}{2}$ atmospheres by making the outlet tube dip under mercury. The crystals are stable at the atmospheric pressure at temperatures below $+5°$; at higher temperatures they decompose, evolving a considerable quantity of acetylene. The compound is a mixed hydrate of acetylene and carbon tetrachloride, and is more stable than the simple hydrate of acetylene. Similar compounds have been obtained by using chloroform, ethylenic chloride, methylic iodide, bromoform, tribromethane, methylenic chloride, or iodide and methylchloroform. Similar compounds may also be obtained by using ethylene, carbonic anhydride, or sulphurous anhydride in place of acetylene.

J. J. S.

Interaction of Cyanides with Thiosulphates. By LEONARD DOBBIN (*Chem. News*, 1898, **77**, 131).—By grinding together potassium cyanide and potassium thiosulphate and leaving them in contact, the change represented by the equation $K_2S_2O_3 + KCN = K_2SO_3 + KCNS$ gradually but completely ensues.

D. A. L.

Dichlorhydrin and Epichlorhydrin. By HUGO FLEMMING (*Chem. Zeit.*, 1897, **21**, 97. Compare Abstr., 1896, i, 333).—Dichlorhydrin, and especially epichlorhydrin, are good solvents for different nitrated celluloses, and also for such substances as celluloid. Gun cotton is readily soluble in epichlorhydrin, but even a 20 per cent. solution is so thick that it requires diluting with alcohol before being used as a varnish. It is suggested that these solvents possess several advantages over the usual solvents employed in the nitrated cellulose industries.

J. J. S.

Melibiose. By A. BAU (*Chem. Zeit.*, 1897, **21**, 185—188).—The author's determinations of the specific rotatory power of melibiose differ somewhat from those made by Scheibler and Mittelmeier (Abstr., 1890, 1085), but in no case has a crystalline material been obtained, so that even these numbers may not be absolutely correct. The melibiose was obtained from melitriose both by acid inversion and by fermentation. As the result of some 24 determinations $[\alpha]_D = +134·25$, or calculated for the ash-free compound $[\alpha]_D = +136·17$. The strength of the different solutions was calculated in most cases from Brix's table of the specific gravities at 17·5°. Scheibler's number is $+126·7 — +126·9°$, and the fact that it is low is probably due to the formation of decomposition products during the boiling with alcohol.

It has been found that moderately concentrated solutions of melibiose have a higher reduction factor than very concentrated solutions, when the boiling is continued for 4 minutes; when boiled for a longer time, a further quantity of cuprous oxide is precipitated. The factor for 4 minutes is about 90—93 per cent. of that for maltose.

Compounds with calcium, barium, strontium, potassium, and sodium have been prepared; these resemble the corresponding derivatives of milk-sugar. It also resembles milk-sugar in its hydrolysis, it is inverted by hydrochloric, sulphuric, or oxalic acid, but not by lactic, tartaric, or citric acid. For inversion by melibiase, compare Abstr., 1896, i, 453. Melibiose is not fermented by *Saccharomyces cerevisiæ*, OF, UF, OS, US; *S. ellipsoideus*, II, Hansen; *S. apiculatus*; *S. Logos* (Van Laer); *Monilia candia*; nor by *Schizosaccharomyces Pombe* (Lindner). Melitriose is not fermented by *Saccharomyces apiculatus*. Melibiose is used technically for determining whether a top yeast is adulterated with a bottom yeast. J. J. S.

Arabinose and Semicarbazide. By WILHELM HERZFELD (*Chem. Centr.*, 1897, ii, 894; from *Zeit. Ver. Rübenzuck.-Ind.*, 1897, 604—605).—When hot solutions of arabinose (1 mol.) and semicarbazide (1 mol.) in 95 per cent. alcohol are mixed, boiled for an hour, and the mixture then evaporated, crystals of *arabinosesemicarbazide*, $C_6H_{13}N_3O_5$, are obtained; this melts and decomposes at 163—164°, is easily soluble in cold water, insoluble in ether, benzene, and chloroform, and dissolves in methylic or ethylic alcohol only on boiling for some time. The rotatory power of an alcoholic solution containing 0·5 gram in 100 c.c. is $-0·35°$, and of an aqueous solution containing 0·1 gram in 50 c.c. $-0·15°$. Benzylidenesemicarbazide is obtained by boiling an aqueous solution of arabinosesemicarbazide with benzaldehyde; after filtering, the solution is dextrorotatory. E. W. W.

Effect of Pressure and Temperature on the Conversion of Starch into Sugar. By FRIEDRICH LIPPMANN (*Chem. Centr.*, 1897, ii, 557; from *Österr. Zeit. Zucker-Ind.*, **26**, 657—668).—The author describes processes of saccharification carried out under pressures obtained by the use of compressed gases, but at temperatures only slightly above 100°. A number of experiments are described in which pure potato-starch was treated with 3 per cent. of its weight of concentrated sulphuric acid diluted with 10 times its volume of water. Heating was effected by blowing in steam, and the various pressures were obtained by using compressed air, carbonic anhydride, or sulphurous anhydride. The results of 8 experiments showed that as the pressure is increased, the diminution in the time required to effect the conversion becomes relatively less and less, and that the most rapid conversion is obtained when the temperature corresponds to the boiling point of the solution at the given pressure. Rise of temperature has much more effect than increase of pressure, but at temperatures above 120—130° the processes of decomposition and recombination about balance. The best results showed on the average a content of about 96 per cent. of dextrose. Other conditions being similar, pressure has little effect on the purity of the product.

E. W. W.

Action of Diastase on Ungelatinised Starch. By Elek von Sigmond (*Chem. Centr.*, 1897, ii, 614; from *Woch. Brauerei*, **14**, 412).—According to the author, the results obtained by Lintner's method (*Woch. Brauerei*, 1890, 22) are uncertain if the mixture is not stirred. From experiments in which a mixture of 2 grams of starch with 50 grams of water and 50 c.c. of malt extract were kept stirred, the author finds that the temperatures of gelatinisation and of solution of potato-starch are identical, namely, 65°; for maize-starch these temperatures are 68° and 70° respectively; for rice-starch, 72° and 83°; for wheat-starch, 62° and 60—65°, and for rye-starch, 55° and 55—60° respectively. When potato-starch is heated with diastase at 65°, 93·06 per cent. is inverted; under similar conditions, 63·5 of maize-starch, 25·3 of rice-starch, 94·26 of wheat-starch, and 91·28 per cent. of rye-starch undergo this change. The author is unable to confirm Lintner's statement with reference to the similarity of the behaviour of maize- and rice-starch, and finds, moreover, that wheat-starch is more readily attacked at 60° than rye-starch. E. W. W.

A New Carbohydrate. Caroubin. By Jean Effront (*Compt. rend.*, 1897, **125**, 38—40).—The grain of *Ceratonia siliqua* has the following composition:—Water, 11·40; nitrogenous matter, 18·92; carbohydrates, 62·00, and fatty matter, 2·3 per cent. The nitrogenous matter is very unequally distributed in the grain. The carbohydrates of the albumen are completely absorbed during germination, whilst those of the spermoderm are not. The carbohydrate of the albumen, for which the author suggests the name *caroubin*, resembles to a certain extent *d*-galactan, but differs from it in its products of hydrolysis; its method of extraction is given in detail. It is a white, spongy, friable substance having the same percentage composition as cellulose. Placed in contact with water, or with normal sodium hydroxide, it forms a jelly or transparent viscid mass, the addition of 3—4 grams of the substance to a litre of water giving the liquid the consistency of a thin syrup. Cold hydrochloric acid dissolves it, but the liquid does not reduce Fehling's solution. With hot nitric acid, it yields levulinic acid. Dilute warm mineral acids hydrolyse the carbohydrate, yielding a dextrogyrate solution which has strong reducing properties.

J. J. S.

Theory of the Sulphite Process and the Constitution of Lignin. By Peter Klason (*Bied. Centr.*, 1898, **27**, 138; from *Svensk kem. tidskr.*, 1897, **9**, 135—138).—When coniferin is heated at 108° with calcium hydrogen sulphite, the coniferylic alcohol combines with the sulphite, forming a salt of the dibasic coniferylsulphonic acid. This can only be explained on the assumption that the alcohol of the coniferin contains the group $-CH_2\cdot\underset{\diagdown O \diagup}{CH\cdot CH_2}$, and the ring being necessarily broken when the sugar is eliminated, an unsaturated compound, or else polymerisation, results.

The behaviour of the lignin of pine wood (lignylglycide) indicates that it is also a glucoside containing an aromatic group. It contains, besides methoxyl, hydroxyl, and active carbonyl groups. The number

of carbon atoms it contains is between 18 and 22. When wood containing lignin is boiled with calcium hydrogen sulphite, the lignylglycide is converted into readily soluble sulphonate, but when the wood is treated with dilute mineral acids, the lignylglycide is converted into a dark-coloured resin containing about 40 carbon atoms.

N. H. J. M.

Methylhydroxyethylamine and Methyldihydroxydiethylamine. By LUDWIG KNORR and HERMANN MATTHES (*Ber.*, 1898, **31**, 1069—1072. Compare Abstr., 1889, 1218).—Methylhydroxyethylamine and methyldihydroxydiethylamine have now been prepared pure by the method previously described (Abstr., 1897, 313). Methylhydroxyethylamine boils at 159°, is a colourless, strongly basic oil, with a characteristic odour, fumes in the air, has a sp. gr. = 0·9370 at 20°/4°, and an index of refraction $n_D = 1·4385$ at 20°, and is miscible with water, alcohol, and ether. It yields precipitates with mercuric chloride, phosphomolybdic acid, and potassium bismuthiodide. The *picrate* forms slender, matted needles melting at 148—150°; the *aurochloride* crystallises in anhydrous prisms melting at 145—146°, and the *platinochloride* in compact tablets decomposing at 125—130°.

Methyldihydroxydiethylamine is a thick, colourless, strongly basic oil which fumes in the air, boils at 246—248° (corr.) under a pressure of 747 mm., and is miscible with water and alcohol, but is only sparingly soluble in ether. It has a sp. gr. = 1·0377 at 20°/4°, and an index of refraction $n_D = 1·4678$ at 20°. It yields precipitates with mercuric chloride phosphomolybdic acid, tannin, and potassium bismuthiodide. The *picrate* melts at 94—95°, and the *aurochloride* at 101—102°, whilst the *platinochloride* decomposes at 148—150°.

A. H.

Alcohol Bases from Ethylamine. By LUDWIG KNORR and WERNER SCHMIDT (*Ber.*, 1898, **31**, 1072—1077).—Ethylene oxide reacts vigorously with ethylamine, forming a mixture of hydroxydiethylamine and dihydroxytriethylamine, which can be separated by fractional distillation. *Hydroxydiethylamine*, $OH·CH_2·CH_2·NHEt$, is a colourless, strongly basic oil, which has a faint odour, and boils at 167—169° (corr.) under a pressure of 751 mm., its vapour fuming strongly in the air. It is easily soluble in water, alcohol, and ether, and readily attacks copper and brass, as well as organic tissues. It has a sp. gr. = 0·9140 at 20°/4°, and a molecular refraction = 25·66, the index of refraction, n_D, being 1·4440 at 20°. It yields characteristic precipitates with mercuric chloride, phosphomolybdic acid, potassium cadmio-iodide, tannin, and potassium bismuthiodide.

The *hydrochloride* forms lustrous, deliquescent needles, whilst the *aurochloride* crystallises in light yellow needles melting at 127°, and the *platinochloride* forms deliquescent crystals which decompose at about 146°. The *picrate* crystallises in pale yellow, monosymmetric prisms melting at 125—127°.

Dihydroxytriethylamine, $NEt(CH_2·CH_2·OH)_2$, is a yellowish oil which has a slight ammoniacal odour, and boils at 251—252° (corr.) under a pressure of 750 mm. It is only sparingly soluble

in ether, is very hygroscopic, and readily attacks copper and the epidermis, but has little action on cork; the sp. gr. = 1·0135 at 20°/4°, and the molecular refraction = 36·37, the index of refraction, n_D, being 1·4663 at 20°. The base yields characteristic precipitates with mercuric chloride, phosphomolybdic acid, potassium cadmioiodide, tannin, and potassium bismuthiodide. The *picrate* crystallises in yellow fascicular groups of needles melting at 100—101°. The *hydrochloride* forms deliquescent plates, whilst the *aurochloride* crystallises in light orange-yellow prisms melting at 81°, and the *platinochloride*, $(C_6H_{15}NO_2)_2,H_2PtCl_6 + H_2O$, forms flat, orange-yellow hygroscopic prisms which melt at 49—50°, whereas the anhydrous salt melts at 108—110°. The *ethiodide*, $C_6H_{15}NO_2$,EtI, forms lustrous, thin plates melting at 212—214°. A. H.

Relation of Tervalent to Quinquivalent Nitrogen. By ARTHUR LACHMAN (*Amer. Chem. J.*, 1898, **20**, 283—288).—Dimethylnitrosamine and diethylnitrosamine form hydrochlorides which are very unstable salts, readily decomposing at a slightly elevated temperature into nitrosyl chloride and the amine. Diphenylnitrosamine takes up dry hydrogen chloride at ordinary temperatures, with immediate elimination of nitrosyl chloride.

Diethylnitrosamine reacts rapidly with zinc ethyl when heated to 100°, basic gases being given off and tarry matter remaining; but diphenylnitrosamine reacts violently with zinc ethyl to form an amorphous, yellow additive product of unknown composition, melting at about 135°. Water converts it into zinc hydroxide, diphenylamine, and an unstable base which reduces Fehling's solution.

When hydroxylamine acts on diphenylnitrosamine, an additive product is formed which at once decomposes into nitrous oxide and diphenylamine.

It appears that, in all these cases, the quinquivalent nitrogen compound readily splits up into simpler substances containing tervalent nitrogen. A diversity among the attached groups is necessary for the existence of quinquivalent nitrogen, for no compound is known in which all five radicles are alike in chemical character, and all attempts to prepare such a compound have proved abortive. A. W. C.

Diacetonehydroxylamine, and Stereoisomeric Aliphatic Ketoximes. By CARL D. HARRIES and LUDWIG JABLONSKI (*Ber.*, 1898, **31**, 1371—1384. Compare this vol., i, 121).—The absence of stereoisomerism among the oximes of unsymmetrical aliphatic ketones has been already the subject of remark (compare Meyer and Scharvin, Abstr., 1897, i, 612), but no satisfactory explanation of the circumstance has been put forward. The authors have found that the oxime of mesitylic oxide is an exception to this rule, being capable of existence in two forms, which probably owe their isomerism to steric influences.

Another ketone having an ethylenic linking in the $\alpha\beta$-position has been shown to yield isomeric oximes; methylcyclohexenoneoxime, prepared by Hagemann, melts at 88—89° (Abstr., 1893, i, 393), whilst the substance described by Knoevenagel (Abstr., 1895, i, 48) melts at 50—60°. The authors have heated the hydrochloride of the latter

form at 80°, obtaining in this manner the salt of the other modification; they therefore regard the oxime having the higher melting point as the analogue of stable mesityloxime, the more readily fusible derivative corresponding to labile mesityloxime.

Diacetonehydroxylamine, $OH\cdot NH\cdot CMe_2\cdot CH_2\cdot COMe$, is prepared by the action of hydroxylamine on mesitylic oxide in presence of sodium methoxide, and is purified by conversion into the oxalate; it crystallises from light petroleum, melts at 52°, and boils at 94—95° under a pressure of 9—10 mm. The substance is very hygroscopic, dissolving in water and organic solvents; it reduces Fehling's solution immediately when gently heated. The *oxalate*, which crystallises from a mixture of alcohol and ether, and melts at 145—147°, is extremely soluble in absolute alcohol; the *picrate* melts at 107—108°, the *hydrochloride* is hygroscopic, and the *platinochloride* and *aurochloride* crystallise slowly in six-sided prisms. The *benzoyl* derivative crystallises in lustrous leaflets, and melts at 165°; it dissolves in dilute caustic soda, and does not reduce Fehling's solution. The *phenylthiocarbamide* crystallises from light petroleum, and melts at 110—112°; when gently heated, it reduces Fehling's solution, and when boiled with caustic soda yields mesitylic oxide. Reduction with sodium amalgam converts diacetonehydroxylamine into diacetonealkamine.

β-Nitrosoisopropylacetone, $NO\cdot CMe_2\cdot CH_2\cdot COMe$, obtained by boiling a solution of diacetonehydroxylamine in chloroform with mercuric oxide in a reflux apparatus, crystallises in stout, white prisms, and melts to a blue liquid at 75—76°; it is highly volatile, and has a pungent, irritating odour.

Dinitrosodi-isopropylacetone, $CO(CH_2\cdot CMe_2\cdot NO)_2$, is prepared by oxidising triacetonedihydroxylamine under the same conditions; it crystallises from benzene or from toluene, and melts at 132—133° to a deep blue liquid.

3 : 5 : 5-*Trimethyldihydroisoxazole*, $\begin{matrix} CMe\text{---}O \\ \Vert \\ CH\cdot CMe_2 \end{matrix}\!\!>\!NH$, is another product of the action of hydroxylamine on mesitylic oxide in presence of sodium methoxide; it is a mobile, highly refractive liquid which boils at 52° and 162—164° under pressures of 9 mm. and 760 mm. respectively.

a-Mesityloxime, $CMe_2{:}CH\cdot CMe{:}NOH$, boils at 85° under a pressure of 10 mm.; it dissolves readily in dilute acids and alkalis, and resists the action of Fehling's solution. The *hydrochloride* is prepared by passing dry hydrogen chloride into an ethereal solution of the fraction of the oxime which boils at 92—94°, under a pressure of 15 mm., this fraction having been obtained by the action of free hydroxylamine on the ketone; on adding dry ether to the solution in absolute alcohol, it crystallises in regular, four-sided plates. The salt has no definite melting point, but sinters below 55° and melts at about 62°, although solid fragments remain suspended in the liquid at about 70°; at 80°, it suddenly becomes solid, being converted into the hydrochloride of the stable form.

β-Mesityloxime melts at 48—49°, resembling the labile modification in chemical properties; it boils at 92° and 102° under pressures of 9 mm. and 13 mm. respectively. The *hydrochloride*, prepared in the

manner already described, and also by the action of hydroxylamine hydrochloride on mesitylic oxide, crystallises in long needles, and melts and decomposes at 123°. The salt is produced when a solution of the labilesalt in absolute alcohol is allowed to remain during two days.

The stable modification of methylcyclohexenoneoxime is obtained when hydroxylamine hydrochloride (1 mol.) acts on methylcyclohexenone. When two molecular proportions are employed, the *compound*, $C_7H_{14}N_2O_2,H_2O$, is produced; this crystallises from hot water in four-sided prisms, and melts at 83—84°. Its behaviour towards mercuric oxide, which converts it into a deep blue nitroso-derivative, shows the substance to be a hydroxylamino-oxime. M. O. F.

Alkylic Isocyanates [Carbimides] and Heat of Formation of Liquid Cyanic Acid. By PAUL LEMOULT (*Compt. rend.*, 1898, **126**, 43—45).—In the preparation of alkylcarbimides (alkylic isocyanates) by Wurtz's method, it is necessary to use potassium cyanate which has been recently prepared, and to take care that all the compounds used are free from water. 100 grams of potassium cyanate and 200 grams of sodium ethyl sulphate give about 12 grams of pure ethylic isocyanate; a quantity of the polymeride is formed at the same time.

Methylcarbimide, CO:NMe, is a colourless liquid boiling at 40°, and polymerising with the greatest readiness. The molecular heat of combustion at constant volume is 268·9 Cal., and at constant pressure 269·3 Cal; the molecular heat of formation at constant pressure is +22·8 Cal. Ethylcarbimide boils at 60°. Its molecular heat of combustion at constant volume is 424·2 Cal., and at constant pressure 424·4; its molecular heat of formation is +31 Cal. It follows from these numbers that the two compounds are true homologues. The heat evolved during polymerisation of methylcarbimide is 34·7 Cal., and for ethylcarbimide 34·9 Cal; taking the mean of these two numbers, and subtracting it from the heat of formation of cyanuric acid (55·45 Cal.) it gives 20·65 Cal., which should be the heat of formation of liquid cyanic acid. J. J. S.

Bromacraldehyde and Tribromopropaldehyde. By OSCAR PILOTY and ALFRED STOCK (*Ber.*, 1898, **31**, 1385—1388).—*Bromacraldehyde*, CH_2:CBr·CHO, prepared by the action of a boiling, aqueous solution of sodium acetate on dibromopropaldehyde, is a colourless, mobile liquid having an intensely irritating smell, and gradually undergoes decomposition with development of a yellow coloration. The substance boils at 28·5°, 37°, 49°, and 111° (corr.), under pressures of 11 mm., 14 mm., 27 mm., and 420 mm. respectively, slowly undergoing decomposition when distilled under atmospheric pressure; it has the sp. gr. = 1·68°. The aldehyde is neutral to litmus, and dissolves somewhat readily in warm water, more sparingly, however, in cold; it reduces Fehling's solution vigorously when heated.

Tribromopropaldehyde, $CH_2Br·CBr_2·CHO$, is the product of the action of bromine on the foregoing substance; it has the sp. gr. = 2·51, and remains unchanged when protected from light, which turns it yellow. It boils at 85·5° (corr.) under a pressure of 11 mm., but under atmospheric pressure it decomposes above 155°, yielding

hydrogen bromide. The aldehyde dissolves with difficulty in cold water, but is miscible with ether, benzene, methylic alcohol, and ethylic alcohol, generating heat with the latter. When exposed to air, it absorbs moisture, yielding the *hydrate* which contains $2H_2O$ and crystallises from water in large rhombic plates; it melts at 55—57°, and reduces Fehling's solution when heated. M. O. F.

A New Cyclic Ketone. Δ^6-Methylcyclohexenone-3. By AUGUSTE BÉHAL (*Compt. rend.*, 1898, **126**, 46—49).—The benzoyl derivative, melting at 167°, from the ketone isolated from wood oil, when treated with alkalis, gives an oxime melting at 121·5°, and this, on hydrolysis with hydrochloric acid, yields a *ketone*, $C_7H_{10}O$, boiling at 192° and melting at 12°. It does not combine with sodium hydrogen sulphite, or yield iodoform on treatment with iodine and alkalis. In carbon bisulphide solution, it readily combines with bromine, yielding a *dibromide* which is easily soluble in warm alcohol or light petroleum. The ketone reacts with phosphorus pentachloride, yielding a deep greenish-blue liquid, which, when distilled in steam, yields a small quantity of a heavy oil with an odour resembling that of terebenthene, a small quantity of a crystalline product and the regenerated ketone. When oxidised with permanganate, the ketone yields acetic and levulinic acids only. The author considers these reactions best agree with the formula for the ketone, $CMe{<}{}^{CH\cdot CH_2}_{CH_2\cdot CO}{>}CH_2$. J. J. S.

Alkylic Salts of Chlor- and Brom-acetic Acid. By RUDOLF L. STEINLEN (*Chem. Centr.*, 1897, ii, 659; from *Bul. Acad. roy. Belg.*, [iii], **34**, 101—108).—*Propylic chloracetate* is an oil of an ethereal odour, of sp. gr. = 1·0944 at 15°/4°, and boils at 149°. *Butylic chloracetate* is a colourless liquid of sp. gr. = 1·0675 at 15°/4°, boils at 170°, and has an odour similar to the preceding salt. *Propylic bromacetate* is a colourless liquid which soon becomes dark, has a sp. gr. = 1·4166 at 15°/4°, and 1·4099 at 20°/4°, and boils at 178° under 765 mm. pressure; its vapour, like that of the following salts, has a very irritating action on the eyes. *Isopropylic bromacetate* is a yellowish oil, of sp. gr. = 1·399 at 15°/4°, and boils at 165·5° under 769 mm. pressure. *Isobutylic bromacetate* is a yellowish oil which rapidly becomes dark, boils at 188° under 752 mm. pressure, and has sp. gr. = 1·3327 at 15°/4°, = 1·3269 at 20°/4°. All these substances are insoluble in water and soluble in alcohol and ether.

A table is given showing how the substitution of chlorine by bromine in the analogous alkylic salts of chloracetic or bromacetic acid raises the boiling point regularly by 16—18°. E. W. W.

Effect of Temperature on the Acidity of Acids. By PAUL DEGENER (*Chem. Centr.*, 1897, ii, 936; from *Festschrift Techn. Hochschule Braunschweig*, 1897, 451—464).—When asparagine is titrated with normal alkali in the cold, using unneutralised phenolphthalein as indicator, only 0·264 equivalent of alkali is required for each molecule of acid, and if the solution is then heated to 100°, a further quantity of 0·540 equivalent of alkali is necessary to neutralise the solution. If the solution is heated to 100° before titrating, 0·96 equi-

valent of alkali is required, and, on cooling, the solution becomes alkaline, and, when cold, 0·69 equivalent of sulphuric acid must be added to destroy the red coloration. Ammonia is not liberated when the solutions are heated, and the author attributes this change in acidity to the decomposition of more complex molecules, and not to the hydrolysis of the asparagine. Aspartic acid requires 0·94 equivalent of alkali at 0°, and 1·208 at 100°; the hot neutralised solution becomes alkaline on cooling, and, "after neutralising the excess required 1·024—1·058 equivalents of alkali." (?) To neutralise sulphurous acid in the cold, 15·6 per cent. more alkali than is necessary to form K_2SO_3 must be added, and, when heated, the solution becomes alkaline. According to the author, orthosulphurous acid, $S(OH)_4$, is present in the cold solution, and this, when the solution is warmed, decomposes into sulphurous acid and water.

Butyric acid at 0° takes up 97·9, and at 100°, 98·55 per cent. of the calculated amount of alkali; the change of colour is sharp, as is generally the case with acids which contain no hydroxyl groups. Acetic and oxalic acids combine with the theoretical quantity of alkali, both in the cold and when heated. Glutaric acid requires 77—77·5 c.c., and succinic acid, both at 0° and at 100°, 101·7 c.c., instead of 100 c.c. Lactic acid at 0° takes up only sufficient alkali to combine with the carboxyl groups, but, at 100°, 9—12 per cent. more is used. Malic acid requires 93·4 c.c. in the cold, and 95·0 c.c. at 100°, instead of 92·0 c.c., and tartaric acid, when warmed, requires 101 c.c. instead of 100 c.c. In the case of these hydroxy-acids, and also of citric acid, probably some alkali is used to combine with the hydroxyl groups. When tartaric acid is dried at 100°, and a solution of it then at once titrated, only 60 c.c. of alkali are required in the cold, and 89·5 c.c. when heated. According to the author, this is due to the formation, without loss of weight, of an internal anhydride, which is only slowly hydrolysed. Citric acid dried at 100° behaves in a similar way. Phosphoric acid in the cold combines with 63 per cent. of the alkali necessary to form the tribasic phosphate. E. W. W.

δ-Amidovaleric Acid. By HEINRICH SALKOWSKI (*Ber.*, 1898, 31, 776—783).—A sample of δ-amidovaleric acid obtained in the putrefaction of glue was compared with a sample prepared synthetically by oxidising benzoylpiperidine with potassium permanganate, and hydrolysing the product with hydrochloric acid (Schotten, Abstr., 1888, 1104), and with another obtained years before (Abstr., 1883, 925) in the putrefaction of fibrin and flesh. The aurochlorides had the same melting point and crystalline form [monoclinic; $a:b:c = 1·1756:1:1·0043$; $\beta = 48° 23' 40''$]; the benzoyl derivatives melt at the same temperature, which is 105·1°, as determined by a thermometer immersed in the solidifying substance.

When the orange aurochloride, $C_5H_{11}NO_2,HAuCl_4 + H_2O$, is recrystallised from water, a yellow salt, with the unusual composition $C_5H_{11}NO_2,AuCl_3$, is obtained; this can also be obtained, although with difficulty, by the direct combination of $AuCl_3$ with amidovaleric acid. Recrystallisation from dilute hydrochloric acid reconverts it into the original aurochloride. C. F. B.

Use of Zinc Oxide in the Preparation of Fermentation Lactic Acid. By JOHANNES GADAMER (*Chem. Centr.*, 1897, ii, 937; from *Apoth.-Zeit.*, **12**, 642—643).—The author attributes Kassner's failure to obtain lactic acid by fermenting a solution of sugar in presence of zinc oxide (this vol., i, 296) to his using a large quantity of old cheese, which does not induce energetic fermentation, instead of sour milk, which contains abundant lactic acid bacteria. When the latter is employed, zinc dextrolactate is obtained. Calcium carbonate, which Kassner used instead of zinc oxide, is probably a favourable material for the growth of lactic acid bacteria. Commercial lactic acid is either inactive or dextrorotatory. E. W. W.

Autoracemisation. By PAUL WALDEN (*Ber.*, 1898, **31**, 1416—1422. Compare this vol., i, 178).—The author has repeatedly shown that, under the influence of heat, the specific rotatory power of halogen substituted ethereal salts readily undergoes change. Data are collected in the present paper showing that compounds of a certain class exhibit diminution of rotatory power after lapse of time, without being submitted to external influences. Of the compounds which have been examined, methylic *d*-bromosuccinate, ethylic *d*-bromosuccinate, isopropylic *d*-bromosuccinate, isobutylic *d*-bromosuccinate, methylic *d*-phenylbromacetate, isobutylic *d*-phenylbromacetate, and *d*-phenylbromacetic acid exhibit this phenomenon, which, however, is not shown by propylic *d*-bromosuccinate, methylic *d*-chlorosuccinate, isopropylic *d*-chlorosuccinate, methylic acetylmalic acid, ethylic isobutyrylmalic acid, methylic *d*-chloropropionate, ethylic *d*-phenylchloracetate, ethylic *l*-mandelate, and ethylic isovaleryl-*l*-mandelate.

The author recognises the following points.

1. There exist active compounds, particularly bromine substituted compounds of succinic, propionic, and phenylacetic acids, which exhibit a decrease of rotational activity if kept for a considerable period; in some cases, the rotatory power is completely lost, and the change in question is associated with both liquid and solid states.

2. The diminution or loss of activity is spontaneous, and proceeds without decomposition on the part of the active substance, the composition, and such physical constants as boiling point, density, and refractive index, undergoing no change.

3. The alteration is permanent, and neither fractionation nor crystallisation of the product is capable of restoring the original rotation.

4. The phenomenon depends on the structure of groups which enter compounds of the same type, shown by the difference in behaviour of propylic and isopropylic *d*-bromosuccinates; it is also associated with the nature of the four groups attached to the asymmetric carbon atom, being non-existent in the case of hydroxy-compounds, hardly recognisable among chloro-derivatives, although well defined in the case of bromo-compounds. M. O. F.

Partial Racemism. By ALBERT LADENBURG and W. HERZ (*Ber.*, 1898, **31**, 937—938).—The solubility of the quinine salt of *l*-pyrotartaric acid in alcohol has now been determined, and it has been found that 100 parts of alcohol dissolve 15 parts of this compound, 4·2 parts of the salt of the dextro-acid, and 3·2 parts of the salt of the inactive

acid. From this it follows that the salt of the inactive acid is not a mixture of the salts of the dextro- and lævo-acids, but is an individual salt derived from the racemic acid. A. H.

A Method of Preparing Ethylic Alkylideneacetoacetates. By EMIL KNOEVENAGEL (*Ber.*, 1898, **31**, 730—737).—It has been shown that benzaldehyde (1 mol.) will react at a low temperature with ethylic acetoacetate (1 mol.), under the influence of a little piperidine, forming ethylic benzylideneacetoacetate, CHPh:CAc·COOEt (Abstr., 1896, i, 232). This will react with a second molecule of ethylic acetoacetate, yielding ethylic benzylidenediacetoacetate, $CHPh(CHAc·COOEt)_2$ (Hantzsch, Abstr., 1886, 77; Knoevenagel, Abstr., 1896, i, 210). More examples of these reactions have been investigated, both aromatic and aliphatic aldehydes being used. The aldehyde and ethylic acetoacetate were usually mixed at $-10°$ to $-15°$, a small quantity of piperidine was added, one drop at a time and at intervals of several minutes, and the mixture was then allowed to remain at the same temperature, sometimes for a day or two. In some cases the product crystallised out; if it did not, the mixture was washed with dilute sulphuric acid (to remove piperidine) and then with water, dried over dehydrated sodium sulphate, and distilled under diminished pressure. The aldehydes experimented with were cuminaldehyde, orthonitrobenzaldehyde, salicylaldehyde, furfuraldehyde, cinnamaldehyde, acetaldehyde, isobutyraldehyde, isovaleraldehyde, and œnanthaldehyde. Most of the acetoacetates had been obtained before by the use of other condensing agents, such as acetic anhydride or hydrochloric acid; the diacetoacetates obtained were also known previously.

The following compounds, or boiling points, are new, however. *Ethylic cumylideneacetoacetate*, boiling at 198° under 10 mm. pressure. *Ethylic cinnamylideneacetoacetate*, boiling at 213—214° under 17 mm. pressure. *Ethylic œnanthylideneacetoacetate*, boiling at 145° under 10 mm. pressure, and with sp. gr. = 0·9647 at 21°. Acetylcoumarin is the product when salicylaldehyde is used; it, as well as its phenylhydrazone (the hygroscopic sodium salt of which melts at 160°) and oxime were described (Arnot, *Inaug.-Diss.*, Heidelberg, 1896) before the publication of Rap's results (*Gazzetta*, 1897, **27**, ii., 498; this vol., i, 317). Ethylic ethylideneacetoacetate boils at 107°, 101°, 96°, and 94° under pressures of 20, 15, 11 and 9 mm. respectively. Ethylic isobutylideneacetoacetate boils at 118—124° under 12 mm., ethylic isoamylideneacetoacetate at 136—138° under 9 mm. pressure, and has a sp. gr. = 0·9623 at 21·5°. C. F. B.

Syntheses by the Aid of Ethylic Cyanosuccinate. By LÉONCE BARTHE (*Compt. rend.*, 1897, **125**, 182—183).—A mixture of sodium (3·45 grams), alcohol (150 c.c.), and ethylic cyanosuccinate (30 grams) is added to trimethylenic bromide, and the mixture heated in a reflux apparatus for 5 hours on the water bath. After distilling off the alcohol, the residue is well washed with water and purified by distillation under diminished pressure, or by crystallising from alcohol. The product, *ethylic* $\beta\beta_1$-*dicyanoheptane*-$\alpha\alpha_1\beta\beta_1$-*tetracarboxylate* (3 : 7-*dicyanononanedioate*-3:7-*dimethyloate*), $CH_2[CH_2·C(CN)(COOEt)·CH_2·COOEt]_2$,

crystallises in white, silky crystals melting at 69° and boiling at 215° under 75 mm. pressure.

When a solution of sodium (2·9 grams) in absolute alcohol is mixed with ethylic cyanosuccinate (25 grams), then added to ethylic α-bromisobutyrate (24 grams), and the reaction completed by heating for 3 hours on the water bath; the product isolated as described above is a colourless oil boiling at 233—235° under 25 mm. pressure, and is *ethylic cyanodimethyltricarballylate*,

$$COOEt\cdot CMe_2\cdot C(CN)(COOEt)\cdot CH_2\cdot COOEt.$$

J. J. S.

The Naphthenes of Russian Petroleum. By OSSIAN ASCHAN (*Chem. Zeit.*, 1897, 21, 242, and 287—288).—A *résumé* of work previously published by the author and others. Compare Abstr., 1883, 564; 1884, 1276; 1887, 648, 922; 1891, 1053, 1481; 1892, 847, 1182, 1310, 1311; 1895, i, 339, 411, and 1896, i, 210, 286, 350.

The conclusion arrived at is that these naphthenes are probably mixtures, and they are not, as was previously supposed, reduction products of benzene hydrocarbons but probably contain pentamethylene derivatives. J. J. S.

Reduction of Benzylaminecarboxylic Acids. By ALFRED EINHORN [and JOSEF BRANTL] (*Annalen*, 1898, 300, 156—179. Compare Abstr., 1896, i, 551).—*Orthomethylolhexahydrobenzoic acid* (exo-*hydroxyhexahydro-orthotoluic acid*), $OH\cdot CH_2\cdot C_6H_{10}\cdot COOH$, is the chief non-nitrogenous product of reducing orthodiethylbenzylaminecarboxylic acid with amylic alcohol and sodium, and is also obtained by the reduction of phthalide; it crystallises from benzene in aggregates of small, prismatic needles, and melts at 112°. The *sodium* and *barium* salts crystallise in needles, the *methylic* salt boils at 155° under a pressure of 18 mm., and the *ethylic* salt at 160—162° under a pressure of 32 mm. *Ethylic orthochloromethylhexahydrobenzoic acid*,

$$CH_2Cl\cdot C_6H_{10}\cdot COOEt,$$

boils at 145—147° under a pressure of 15 mm. When oxidised with potassium permanganate, orthomethylolhexahydrobenzoic acid is converted into *trans*-hexahydrophthalic acid.

In addition to *exo*-hydroxyhexahydro-orthotoluic acid, reduction of phthalide gives rise to *hexahydrophthalide*, $C_6H_{10}{<}{\substack{CH_2\\ CO}}{>}O$; it is a colourless liquid having an agreeable odour, and it boils at 160—165° under a pressure of 60 mm.

Hexahydro-orthotoluic acid is another product of the reduction of phthalide and *exo*-hydroxyhexahydro-orthotoluic acid, and when distilled with zinc chloride, it yields hexahydrotoluene.

M. O. F.

Compound of Phosphoric Anhydride with Benzene. By H. GIRAN (*Compt. rend.*, 1898, 126, 592—593).—When a mixture of two parts of phosphoric anhydride and three parts of benzene is heated in a sealed tube at 110—120° for several hours, a very unstable, brick-red solid product is obtained which decomposes when exposed to air, but can be kept in an atmosphere of benzene. It is also decomposed

by water, but dissolves without change in alcohol, and when this solution is treated with barium carbonate, a gelatinous mass is formed which, after washing with absolute alcohol and drying at 110—120°, has the composition $C_6H_2P_8O_{20}Ba_2$, and is the barium salt of *benzenetetradimetaphosphoric acid*, $C_6H_2(PO{:}O_2{:}PO{\cdot}OH)_4$, formed by the union of 1 molecule of benzene with 4 mols. of phosphoric anhydride.

The alcoholic solution of the crude acid may be neutralised with barium ethoxide instead of with the carbonate. C. H. B.

The Benzene Ring. By NICOLAI A. MENSCHUTKIN (*Ber.*, 1898, 31, 1423—1429. Compare this vol., i, 186).—A study of the formation of the benzene ring involves the consideration of two questions, namely, the production of a hexatomic ring from an open chain, and the influence on the decomposition velocity of the anilines exerted by the carbon linkings of the ring.

In order to throw light on the first of these questions, the author has compared the velocity constants of the action of allylic bromide on α-pentylamine (1189), hexamethyleneamine (1309), $\alpha\beta$-pentylamine (586), and β-methylhexamethyleneamine (884), and points out that the conversion of an open chain into a hexatomic ring having the same simple linkings between the carbon atoms is not attended with diminution of the velocity constant.

Assuming that the influence exerted by the nature of the union between carbon atoms is the same in a closed ring as in an open chain, it is possible to study the second of the above questions by considering the velocity constants of the anilines. By comparing the velocity constants of propylamine (3783) and allylamine (1903), it will be seen that if Kekulé's formula for benzene is accepted, the constant for aniline should be considerably lower than that of hexamethyleneamine; the same effect would be anticipated if Claus' view of the structure of the benzene ring is accepted, because the velocity constant of $\alpha\alpha$-pentylamine is 270. As a matter of fact, the constants proper to hexamethyleneamine and aniline are 1309 and 68 respectively. Another point of difference which is due to this cause lies in the lower values obtained when anilines are acted on by methylic bromide as compared with allylic bromide, whereas in the aliphatic series the converse generalisation holds good; this is illustrated by the following table (compare also Abstr., 1895, ii, 385).

	C_3H_5Br.	MeBr.
Aniline	68	24
Methylaniline	504	179
Orthotoluidine	54	13
Metatoluidine	445	86
Paratoluidine	96	52
v-Ortho-xylidine	400	51
as-Meta-xylidine	235	30
ψ-Cumidine	174	46

The aromatic amines, such as benzylamine, differ from the anilines,

displaying the characteristics of aliphatic amines to the exclusion of those features which are associated with the benzene ring. Thus the velocity constants of benzylamine, α-phenylethylamine, and ω-mesitylamine, with allylic bromide, are 997, 750, and 1718; with methylic bromide, the constants of benzylamine and ω-mesitylamine are 2722 and 4565 respectively.

Corresponding differences are revealed on comparing the etherification constants of alcohols with those of phenols, and of aliphatic acids with those of aromatic acids. M. O. F.

Carbonates of the Dihydroxybenzenes. By ALFRED EINHORN [and EUGEN LINDENBERG] (*Annalen*, 1898, **300**, 135—155).—When catechol carbonate, $C_6H_4<\begin{smallmatrix}O\\O\end{smallmatrix}>CO$, is recrystallised from absolute alcohol, it becomes in part converted into ethylic catechol carbonate, $OH\cdot C_6H_4\cdot O\cdot COOEt$. It is also decomposed by primary and secondary bases, yielding compounds of the type $OH\cdot C_6H_4\cdot O\cdot CO\cdot NRR_1$. Whilst ethylenediamine gives rise to dicatecholdicarbethylenediamide, $C_2H_4(NH\cdot CO\cdot O\cdot C_6H_4\cdot OH)_2$, hydrazine forms the two compounds dicatecholcarbohydrazide, $N_2H_2(CO\cdot O\cdot C_6H_4\cdot OH)_2$, and catecholcarbohydrazide, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot NH_2$. The latter is of value in detecting aldehydes, with which it forms derivatives of the type $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N\colon CHR$, and possesses the advantage of solubility in alkalis, from which it is separated unchanged by acids; hitherto, however, it has not been induced to combine with ketones, and therefore affords a means of distinguishing between this class of compounds and aldehydes.

Although the conversion of catechol carbonate into ethylic catechol carbonate under the influence of absolute alcohol is complete at 100°, the carbonates of resorcinol and quinol are scarcely changed under these conditions, first undergoing complete conversion when heated at 130° and 160° respectively; the products, however, have not been isolated. With piperidine, resorcinol carbonate yields two compounds, resorcinolcarbopiperidide, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NC_5H_{10}$, which dissolves in alkalis, and resorcinoldicarbodipiperidide, $C_6H_4(O\cdot CO\cdot NC_5H_{10})_2$, which is insoluble in alkalis. Quinol carbonate behaves in a similar manner.

It is probable that the carbonates of resorcinol and quinol are not monomolecular, and the authors therefore represent them by the general formula $(C_6H_4O_2\cdot CO)_x$.

Ethylic catecholcarbonate, $OH\cdot C_6H_4\cdot O\cdot COOEt$, crystallises from a mixture of alcohol and ether in colourless needles and melts at 58°; it has an aromatic odour and a burning taste, and does not develop colour with ferric chloride. Distillation regenerates catechol carbonate with elimination of alcohol.

Amylic catechol carbonate, $OH\cdot C_6H_4\cdot O\cdot COO\cdot C_5H_{11}$, crystallises from petroleum in leaflets and melts at 53°; it has an aromatic odour.

Catecholcarbanilide, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NHPh$, crystallises from alcohol in small, white scales, and melts at 146°. *Catecholcarboparaphenetidide*, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$, crystallises in lustrous leaflets and also melts at 146°.

Catecholcarbophenylhydrazide, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot NHPh$, slowly reduces a cold solution of silver nitrate, and is oxidised by Fehling's solution when gently heated; it crystallises from methylic alcohol in leaflets and melts at 157°.

Dicatecholcarbethylenediamide, $C_2H_4(NH\cdot CO\cdot O\cdot C_6H_4\cdot OH)_2$, is prepared by the action of ethylenediamine on catechol carbonate (2 mols.); it crystallises from absolute alcohol in highly lustrous leaflets and melts at 165·5°.

Catecholcarbodiethylamide, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NEt_2$, which crystallises in beautiful prisms from a mixture of ether and petroleum, melts at 78°, and dissolves without decomposition in dilute caustic soda. It belongs to the monoclinic system. [$a:b:c = 1\cdot2261:1:0\cdot95498$; $\beta = 114° 26'$.]

Catecholcarbopiperidide, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NC_5H_{10}$, crystallises from absolute alcohol in white prisms and melts at 121°. When boiled with alcohol during half an hour, it is resolved into its components, but dissolves without change in cold, dilute, caustic alkali.

Dicatecholcarbohydrazide, $N_2H_2(CO\cdot O\cdot C_6H_4\cdot OH)_2$, is prepared by adding hydrazine (2·8 grams) to finely powdered catechol carbonate (15 grams), and cooling the clear solution which is produced; on dissolving the crystals in dilute caustic soda, and treating the filtered liquid with hydrochloric acid, the dihydrazide is precipitated, whilst the hydrochloride of the monohydrazide remains in solution. The dihydrazide crystallises from absolute alcohol in colourless plates and melts at 207°.

Catecholcarbohydrazide, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot NH_2$, crystallises from very dilute spirit in white needles, and melts at 154°, becoming solid above this temperature, and finally decomposing at 240°; it is insoluble in benzene and ether, but dissolves in hot alcohol and water. The substance slowly reduces a cold solution of silver nitrate and Fehling's solution when warmed with it; ferric chloride develops a dark coloration. The *acetyl* derivative melts at 180°. The *benzylidene* derivative crystallises from alcohol in colourless needles and melts at 175°; the *orthohydroxybenzylidene* and *parahydroxybenzylidene* derivatives melt at 162° and 175° respectively, the *paramethoxybenzylidene* derivative at 192°. The *ethylidene* derivative melts at 125°; unlike the foregoing products of condensation, this compound undergoes decomposition when dissolved in alkalis.

Resorcinol carbonate, $(C_6H_4O_2{:}CO)_x$, is prepared by passing carbonyl dichloride into a continuously agitated solution of resorcinol in pyridine, cooled with ice; after half an hour the gelatinous precipitate is transferred to water, when the carbonate separates as a white, amorphous powder. It melts and evolves gas at 190°.

Resorcinoldicarbodipiperidide, $C_6H_4(O\cdot CO\cdot NC_5H_{10})_2$, separates in large, transparent plates on adding a few drops of alcohol to the solution in ether; it melts at 122°. *Resorcinolcarbopiperidide*,

$$OH\cdot C_6H_4\cdot O\cdot CO\cdot NC_5H_{10},$$

is soluble in alkalis, and crystallises from a mixture of ether and petroleum in colourless prisms. It melts at 107°.

Quinol carbonate, $(C_6H_4O_2{:}CO)_x$, is insoluble in common solvents and does not melt below 280°.

Quinolcarbopiperidide, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NC_5H_{10}$, which separates on adding ethylic acetate to the alcoholic or ethereal solution, melts at 270°.

Quinolcarbohydrazide, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot NH_2$, is a white, crystalline powder and melts at 168°. M. O. F.

Action of Cyanamide on Bromanil in Presence of Potassium Hydroxide. By H. IMBERT (*Compt. rend.*, 1898, **126**, 529—530).—A solution of cyanamide (8·4 grams), in water (100 grams), is added to finely divided tetrabromoquinone (24·6 grams), the mixture is boiled, and small pieces of potassium hydroxide are added, care being taken that the bromanil remains in excess; the liquid is filtered hot, and as the filtrate cools crystals separate which can be obtained pure after two or three crystallisations from boiling water. The crystals have the form of long needles, some have a green and others a brown appearance, probably the effect of polychroism. Its aqueous solution has a green colour, which changes to violet on the addition of hydrochloric acid; if the acidified solution is shaken with ethylic acetate, the latter assumes a ruby-red colour. Both the green and violet solutions are decolorised by sulphurous anhydride. Analyses point to the compound being *dipotassium dicyanimidodibromdihydroxyquinone*, $CN_2{:}C_6Br_2(OK)_2{:}CN_2 + 2H_2O$. The corresponding *silver* and *barium* compounds have been obtained by double decomposition. Chloranil reacts in a similar manner, and benzoquinone itself gives dicyanimidobenzoquinone. J. J. S.

Veratrylenediamine. By CHARLES MOUREU (*Compt. rend.*, 1897, **125**, 31—34).—Veratrole, when treated at 0—5° with concentrated nitric acid (sp. gr. = 1·48), yields a *dinitro*-derivative crystallising in lemon-yellow needles and melting at 129—130°. The two nitro-groups appear to be in the ortho-position relatively to one another, since on reduction with tin and hydrochloric acid an orthodiamine, *veratrylenediamine*, $C_6H_2(OMe)_2(NH_2)_2$, is obtained; this crystallises in small, colourless prisms melting at 131—132°, and dissolves readily in water, alcohol, or chloroform, but is only sparingly soluble in ether. All its solutions rapidly become dark coloured on exposure to the air, and even the solid base after exposure for several hours assumes a violet colour.

Veratrylphenanthrazine, $C_6H_2(OMe)_2{<}\begin{matrix}N\cdot C\cdot C_6H_4\\ \vert\quad\ \vert \\ N:C\cdot C_6H_4\end{matrix}$, obtained when a warm alcoholic solution of the base (0·84 gram) is added to a boiling acetic acid solution of phenanthraquinone (1·04 grams), crystallises from toluene in small, yellow needles melting at 255°, and gives a violet coloration with sulphuric acid.

Veratrylene-ethenylamidine, $C_6H_2(OMe)_2{<}\begin{matrix}NH\\ N\end{matrix}{>}CMe$, formed when the base is heated for some time with acetic acid, is readily soluble in water, sparingly in ether, and melts at about 170°; its aqueous solution yields precipitates with both platinum chloride and picric acid.

Veratrylbenzaldehydine, $\begin{matrix}CPh\cdot N\cdot CH_2Ph\\ \Vert\qquad \vert\\ N — C_6H_2(OMe)_2\end{matrix}$, is obtained in the form of its hydrochloride when an aqueous solution of veratrylenediamine hydrochloride reacts with benzaldehyde; the *hydrochloride* crystallises

from dilute alcohol in small, colourless needles melting at 134—135°. All these reactions indicate that the base is an ortho-diamine. J. J. S.

Action of Benzoic Chloride on Monosubstituted Orthodiamines. By FERNAND MUTTELET (*Compt. rend.*, 1897, **125**, 107—109). —Substituted ortho-diamines of the type $NO_2 \cdot C_6H_3(NH_2)(NHR)$ [$NHR : NH_2 = 1 : 2 : 4$], where R = phenyl, ortho- or para-tolyl, methyl, α- or β-naphthyl radicles, react with benzoic chloride in two different ways. (1) At a low temperature and in the presence of a solvent such as benzene a benzoyl derivative of the type

$$NO_2 \cdot C_6H_3(NHBz) \cdot NHR$$

is formed. (2). At a high temperature (200°), and in the presence of an excess of the chloride, an inner anhydride of the type

$$NO_2 \cdot C_6H_3 < \begin{matrix} NR \\ —N \end{matrix} \geqslant CPh$$

is produced.

Orthobenzamidoparanitrophenylaniline, $NO_2 \cdot C_6H_3(NHBz) \cdot NHPh$, crystallises from alcohol in yellowish brown needles melting at 201—202°. *Orthobenzamidoparanitroparatolylaniline* forms yellow needles melting at 210—211°; *orthobenzamidoparanitroorthotolylaniline* melts at 164—165°, and *orthobenzamidoparanitro-β-naphthylaniline* melts at 217—218°.

The *anhydride*, $NO_2 \cdot C_6H_3 < \begin{matrix} NPh \\ —N \end{matrix} \geqslant CPh$, is obtained when paranitro-orthamidophenylaniline (1 part) is heated with benzoic chloride (2 parts), first gently and then at about 210—215°, in an oil bath until hydrogen chloride ceases to be evolved; when cold, the mass is treated with sodium carbonate, and, after boiling, the insoluble portion is washed with hot water and recrystallised from boiling alcohol; it crystallises in needles melting at 181°.

The following is a list of the anhydrides which have been obtained in a similar manner.

R = Paratolyl, colourless needles melting at 177—178°.
R = Orthotolyl, yellowish needles melting at 172—173°.
R = α-Naphthyl, small yellow crystals melting at 171—173°.
R = β-Naphthyl, yellow needles melting at 177—178°.
R = Methyl, yellow crystals melting and decomposing at 140°.

J. J. S.

A New Group of Amidines. By FERNAND MUTTELET (*Compt. rend.*, 1897, 125, 243—245).—When the anhydrides obtained by the action of benzoic chloride on monosubstituted orthodiamines (see preceding abstract) are reduced with tin and hydrochloric acid, amidines of the type $NH_2 \cdot C_6H_3 < \begin{matrix} NR \\ —N \end{matrix} \geqslant CPh$ are formed.

R.	Melting point of product.
Phenyl	191°
Paratolyl	193°
Orthotolyl	145—146°
β-Naphthyl	195°

A hydrate of the phenyl derivative containing $1H_2O$ has been obtained, it melts at 172—173°; the corresponding hydrate of the

β-naphthyl derivative melts at 165—166° losing its water and then melting again at 195°. J. J. S.

Behaviour of Diazomethane towards Nitramines and Aromatic Nitro-compounds. By JOHN LEATHART HEINKE (*Ber.*, 1898, **31**, 1395—1400. Compare Degner and von Pechmann, Abstr., 1897, i, 264).—Diazomethane converts nitrourethane into nitromethylurethane. It has a similar action on nitramine, yielding principally dimethylnitramine, along with the isomeride described by Franchimont and Umbgrove (Abstr., 1897, i, 8); there is also formed the *compound*, $C_5H_{11}NO_4$, which boils at 110—112°, and yields potassium carbonate when treated with alcoholic potash.

The nitro-compounds which have shown themselves to be indifferent towards diazomethane are nitromethane, nitrobenzene, nitrotoluene, parabromonitrobenzene, bromodinitrobenzene, and trinitromesitylene.

Symmetrical trinitrobenzene reacts with diazomethane (4 mols.) liberating nitrogen, and yielding the *compound*, $C_{10}H_{11}N_5O_6$, which crystallises from dilute acetic acid in colourless, rhombic plates, and melts at 194—195°, when it decomposes; it is indifferent towards cold caustic soda, yielding a red solution when the liquid is boiled. The substance gives Liebermann's reaction, and under the influence of acids and alkalis is resolved into nitrous acid and the *base*, $C_{10}H_{10}N_4O_4$, which crystallises from dilute alcohol in white, lustrous plates and melts at 164—165°.

Symmetrical trinitrotoluene yields the *compound*, $C_{10}H_{11}N_5O_6$, which crystallises from dilute acetic acid in yellowish needles, and melts at 177°.

Picric chloride gives rise to the *compound*, $C_9H_8N_5O_6Cl$, which crystallises from dilute acetic acid in bright yellow needles, and melts at 176—177°. Alcoholic hydrogen chloride eliminates nitrous acid, yielding the *base*, $C_9H_7N_4O_4Cl$, which crystallises from dilute alcohol in yellowish needles and melts at 179—180°; the *acetyl* derivative forms colourless needles and melts at 156—157°.

Symmetrical trinitrophenylic acetate acts readily with diazomethane, yielding the *compound*, $C_{11}H_{11}N_5O_7$, which separates from dilute acetic acid in yellowish, hexagonal prisms; it melts at 144°. M. O. F.

Compounds of Phenylhydrazine with Metallic Nitrates. By JOSEPH MOITESSIER (*Compt. rend.*, 1897, **125**, 183—185).—The nitrates of metals of the manganese series combine directly with phenylhydrazine in much the same manner as the corresponding haloids (Abstr., 1897, i, 561, 562; this vol., i, 133). These salts, which give the reactions of phenylhydrazine, and also those of the metal they contain, deflagrate when heated, leaving a residue of the metallic oxide.

Cobalt nitrate phenylhydrazine, $Co(NO_3)_2,2N_2H_3Ph + H_2O$, obtained when an excess of phenylhydrazine is quickly added to a 10 per cent. aqueous solution of cobalt nitrate previously diluted with twice its volume of 95 per cent. alcohol, crystallises in microscopic needles, is sparingly soluble in cold water or alcohol, more readily in hot water, and insoluble in ether or chloroform. When heated, it turns blue, then brown, and does not melt below 260°.

Zinc nitrate phenylhydrazine, $Zn(NO_3)_2,3N_2H_3Ph$, is obtained when a 10 per cent. alcoholic solution of phenylhydrazine is gradually added to a 10 per cent. alcoholic solution of zinc nitrate; the precipitate formed contains zinc oxide, from which it may be freed by boiling with alcohol and allowing it to crystallise. In appearance it resembles boric acid, is soluble in hot water or alcohol, but insoluble in ether or chloroform, and melts and decomposes at 170°.

The *cadmium* salt, $Cd(NO_3)_2,3N_2H_3Ph$, may be obtained in a similar manner by using a 5 per cent. alcoholic solution of cadmium nitrate. It melts at 185° and decomposes at about 190°. The *nickel* derivative, $Ni(NO_3)_2,4N_2H_3Ph$, obtained by quickly adding phenylhydrazine to a 20 per cent. alcoholic solution of nickel nitrate, forms a clear blue precipitate, which is sparingly soluble in chloroform, but insoluble in ether, and deflagrates at 141°. J. J. S.

Action of Halogen-substituted Derivatives of Aliphatic Compounds on Phenylhydrazine. By HEINRICH BRUNNER and KARL EIERMANN (*Ber.*, 1898, 31, 1406—1416. Compare this vol., i, 158).—The action of chloroform on phenylhydrazine gives rise to phenylhydrazine hydrochloride, phenylic isocyanide, benzene, ammonium chloride, hydrogen chloride, and nitrogen; the same products, substituting aniline for benzene, are obtained when a solution of carbon hexachloride in ether is mixed with phenylhydrazine. Carbon tetrachloride yields phenylhydrazine hydrochloride, phenylic isocyanide, hydrogen chloride, aniline, and nitrogen; whilst ethylenic dichloride also gives rise to phenylhydrazine hydrochloride when mixed with the base. Bromoform and phenylhydrazine give the hydrobromide, along with phenylic isocyanide, benzene, hydrogen bromide, ammonium bromide, and nitrogen, the analogous change taking place under the influence of iodoform; ethylenic dibromide produces phenylhydrazine hydrobromide when mixed with the base. When chloral, diluted with 25 volumes of ether, is mixed with phenylhydrazine, nitrogen is liberated, and the hydrochloride of the base produced; the other products of the action are benzoic chloride, phenylic isocyanide, aniline, ammonia, and ammonium chloride (compare also Causse, Abstr., 1897, i, 543).

The *compound*, $C_{28}H_{26}N_7O_2Cl$, obtained on mixing aqueous solutions of phenylhydrazine hydrochloride and chloral hydrate, is a reddish-brown, amorphous substance, readily soluble in alcohol, chloroform, and glacial acetic acid, but dissolving with difficulty in benzene and petroleum; it is insoluble in water and ether. The latter agent precipitates it from the solution in chloroform as a yellowish-red substance, and when separated from alcohol or glacial acetic acid by addition of feebly acidified water it is orange-coloured. It becomes brown at 140°, and chars at 145°. Nitric acid converts it into picric acid, whilst alcoholic potash eliminates ammonia, the odour of isocyanide becoming afterwards perceptible; when heated with zinc dust, it yields ammonia, aniline, and an isocyanide. The *acetyl*, *benzoyl* (two), *silver*, *ethyl*, and *propyl* derivatives are amorphous; an amorphous *compound*, $C_{28}H_{24}N_7Cl_3$, is obtained by the action of phosphorus pentachloride.

The *compound*, $C_{28}H_{26}N_7O_2Br$, prepared from phenylhydrazine hydrochloride and bromal hydrate, is a yellow, amorphous powder, resembling the foregoing compound in chemical behaviour. The *acetyl*, *benzoyl*, *silver*, *ethyl*, and *propyl* derivatives, and the *compound* obtained by the action of phosphorus pentachloride, are amorphous.

The *compound*, $C_{16}H_{16}N_3ClO$, is produced when aqueous solutions of phenylhydrazine hydrochloride and butylchloral hydrate are gently heated; the substance itself, the *acetyl*, *benzoyl*, *silver*, *ethyl*, and *propyl* derivatives, and the *compound* obtained by the action of phosphorus pentachloride, are all amorphous.

The authors discuss the possible constitution of the above-mentioned compounds. M. O. F.

Hydrocinnamide. By MARCEL DELÉPINE (*Compt. rend.*, 1898, **126**, 648—651).—Hydrocinnamide, obtained by the action of ammonia on cinnamaldehyde and melting at 106—108°, is really a hydrate, $2C_{27}H_{24}N_2 + H_2O$, which explains the formation of the hydrochloride and the regeneration of the base from it by the action of ammonia. Hydrocinnamide is therefore analogous in this respect to amarine and anisine. Direct estimation of the water was found to be impracticable owing to the rapid alteration of the compound when heated.

The heat of combustion of hydrocinnamide is 8962·8 cals.; molecular heat of combustion at constant volume, 3450·68 cal.; at constant pressure, 3453·5 cal.; heat of formation −81·2 Cal.; heat of formation of the hydrate (liquid water) −79·4 Cal. It follows that $3C_9H_8O$ liquid $+ 2NH_3$ diss. $= C_{27}H_{24}N_2$ solid $+ 3H_2O$ liquid develops +48·4 Cal. These results show that hydrocinnamide is one of the glyoxalidines, a conclusion which is confirmed by the formation of salts, its basic function being more active than that of amarine; it may therefore be termed cinnamine. It also forms a compound with silver nitrate, and resembles amarine in its behaviour with methylic iodide and benzylic chloride. C. H. B.

The Reduction of Ethylic Orthonitrophenylic Carbonate: Ethylic Orthohydroxyphenylcarbamate. By JAMES H. RANSOM (*Ber.*, 1898, **31**, 1055—1066).—Bender's ethylic amidophenylic carbonate, $NH_2 \cdot C_6H_4 \cdot O \cdot COOEt$, melting at 95° (Abstr., 1887, 38), was prepared by reducing ethylic orthonitrophenylic carbonate by shaking it with tin and strong hydrochloric acid and cooling meanwhile. It is identical with Groenvik's ethylic hydroxyphenylcarbamate, $OH \cdot C_6H_4 \cdot NH \cdot COOEt$, melting at 85° (this Journal, 1877, i, 472), prepared from orthamidophenol and ethylic chloroformate. The true melting point of the substance is 85°; its constitution is probably $C_6H_4 {<}{}^{O}_{NH}{>} C {<}{}^{OH}_{OEt}$. It yields a *benzoyl* derivative,

$$C_6H_4 {<}{}^{O}_{NBz}{>} C {<}{}^{OH}_{OEt},$$

which melts at 75·5°; this can also be obtained from ethylic chloroformate and benzoylorthamidophenol, $OH \cdot C_6H_4 \cdot NHBz$, which is itself best obtained by the action of benzoic chloride (1 mol.) on orthamidophenol (2 mols.) in ethereal solution. When this benzoyl derivative is heated in a bath at 240—245°, alcohol comes over first, then a

small quantity of ethylic benzoate, and, lastly, a fraction which contains *benzoylcarbonylamidophenol*, $C_6H_4<\genfrac{}{}{0pt}{}{-O-}{NBz}>CO$, melting at 173—174°, together with a little carbonylamidophenol (from which the former can be prepared by benzoylation), and a little *benzenylamidophenol*, $C_6H_4<\genfrac{}{}{0pt}{}{O}{N}\geqslant CPh$, which melts at 101—102°, and can also be prepared by distilling benzoylcarbonylamidophenol.

Orthanisidine, when heated with ethylic chloroformate in alkaline aqueous solution, yields *ethylic orthomethoxyphenylcarbamate*, $OMe\cdot C_6H_4\cdot NH\cdot COOEt$, boiling at 180—182° under 26 mm. pressure. A product identical with this ought to be obtained by methylating the original substance mentioned above, if Groenvik's formula for it were correct; this substance could not be made to yield a methylic derivative, however. Ethylic orthomethoxyphenylcarbamate, when treated with bromine in carbon bisulphide solution, yields a *monobromo*-substitution derivative which melts at 101·5—102·5°.

Ethylic paranitrophenylic carbonate can be prepared from paranitrophenol in alkaline solution by the action of ethylic chloroformate, and also by dissolving ethylic phenylic carbonate in fuming nitric acid at 0°; it melts at 67—68°. Unlike the ortho-isomeride, it is reduced by tin and alcoholic hydrochloric acid, in the normal manner, to *ethylic paramidophenylic carbonate*, $NH_2\cdot C_6H_4\cdot O\cdot COOEt$, which melts at 35—36°; the *hydrochloride* of this melts and decomposes at 197°, the yellow *platinochloride* melts at 237°, and the *carbamide* (from the hydrochloride and potassium cyanate) at 149—150°. C. F. B.

Some-N-Phosphines and N-Phosphonium Compounds. By C. A. August Michaelis (*Ber.*, 1898, 31, 1037—1047).—Compounds analogous to those prepared from phosphorus trichloride and piperidine (Abstr., 1895, i, 682) have been prepared with phosphenyl chloride, $PPhCl_2$, and similarly constituted chlorides, instead of phosphorus chloride. These trichlorides react with tetrahydroquinoline also, but the reaction is less energetic, and there is no need to cool with ice, or even to dilute with ether; the products, too, form phosphonium compounds less readily than the analogous piperidine derivatives, and that only with methylic iodide, as a rule. No aliphatic N-phosphines have been obtained as yet.

[With Georg Schlüter].—*Phenyldipiperidine*-N-*phosphine*,

$$(C_5H_{10}N)_2PPh,$$

from piperidine (4 mols.) and phosphenyl chloride (1 mol.) in ethereal solution, melts at 78°. With chlorine gas in light petroleum solution, it yields deliquescent *phenyldipiperidine*-N-*phosphine chloride*,

$$(C_5H_{10}N)_2PPhCl_2;$$

this is converted by water into the *phosphine oxide*, $(C_5H_{10}N)_2PPhO$, which is better prepared, however, by the action of phosphenyl oxychloride, $PPhOCl_2$, on piperidine; it is hygroscopic and melts at 68°. The *phosphine sulphide*, obtained by prolonged heating of the phosphine with excess of sulphur at 130°, melts at 92° and is very stable. With carbon bisulphide, the phosphine first forms a yellowish-white compound, probably $(C_5H_{10}N\cdot CS\cdot S)_2PPh$, which melts at 144°; when

crystallised repeatedly from a mixture of benzene with ether, this loses half its carbon bisulphide, yielding a yellow substance, presumably $C_5H_{10}N\cdot CS\cdot S\cdot PPh\cdot NC_5H_{10}$, which melts at 137°. *Phenyldipiperidinemethylphosphonium iodide* (from the phosphine and methylic iodide at the ordinary temperature), *chloride*, and yellowish-red *platinochloride*, $(C_5H_{10}N)_2PPhMeI$, &c., melt at 167°, 130°, and 178° respectively; the *ethylphosphonium iodide* at 174°, and the yellow, deliquescent *benzylphosphonium chloride* at 204°. The methylphosphonium hydroxide is a syrup; when heated, it loses piperidine and forms methylphenylphosphinic acid, $O\colon PPhMe\cdot OH$.

[With FREUNDLICH.]—*Paratolyldipiperidine*-N-*phosphine*,

$$(C_5H_{10}N)_2P\cdot C_6H_4Me,$$

melts at 80°; the hygroscopic *phosphine oxide*, $(C_5H_{10}N)_2PO\cdot C_6H_4Me$, at 60°; the *phosphine sulphide* at 88°, and the pale yellow compound with carbon bisulphide (2 mols., a compound with $1CS_2$ could not be obtained) at 139°. The *methyl-*, *ethyl-*, *propyl-* and *isobutyl-phosphonium iodides*, $(C_5H_{10}N)_2P\cdot C_6H_4Me,MeI$, &c., melt at 186°, 191°, 197°, and 204° respectively; the *benzylphosphonium chloride* at 125°. By heating the methylphosphonium hydroxide at 150—180°, *paratolylmethylphosphinic acid*, $C_6H_4Me\cdot PMeO\cdot OH$, was obtained; it melts at 120°; its *silver* salt was analysed.

[With CURT ROEBER.]—*Chlorophenyl-*, *anisyl-*, and *phenetyl-dipiperidine*-N-*phosphines*, $(C_5H_{10}N)_2P\cdot C_6H_4R$ [R = Cl; OMe; OEt], melt at 95°, 69° and 84° respectively. They were prepared in the same way as phenyldipiperidine-*n*-phosphine, and resemble that substance in their reactions.

[With J. GROSSHEIM.]—*Tetrahydroquinoline*-N-*phosphine*, $(C_9H_{10}N)_3P$, from tetrahydroquinoline and phosphorous chloride, melts at 202—204°, and is decomposed by acids into tetrahydroquinoline and phosphorous acid; it cannot readily be oxidised, but the *phosphine oxide*,

$$(C_9H_{10}N)_3PO,$$

is obtained by the action of tetrahydroquinoline on phosphorus oxychloride; it melts at 90—91°. The N-phosphine (1 mol.) will unite with sulphur (1 mol.), however, at 170°, but not very readily; the resulting *phosphine sulphide*, $(C_9H_{10}N)_3PS$, crystallises in the regular system and melts at 192°. *Tetrahydroquinolinemethylphosphonium iodide*, *chloride*, and reddish-yellow *platinochloride*, $(C_9H_{10}N)_3PMeI$, &c., melt at 188°, 148—150°, and 230° respectively.

Phenylditetrahydroquinoline-N-*phosphine*, $(C_9H_{10}N)_2PPh$, from tetrahydroquinoline and phosphenyl chloride, melts at 150°; the *phosphine oxide*, $(C_9H_{10}N)_2PPhO$, at 216°, and the *methylphosphonium iodide*, $(C_9H_{10}N)_2PPhMeI$, at 136°.

Paratolylditetrahydroquinoline-N-*phosphine*, $(C_9H_{10}N)_2P\cdot C_6H_4Me$, melts at 140°, the *phosphine oxide*, $(C_9H_{10}N)_2PO\cdot C_6H_4Me$, at 181°.

C. F. B.

Behaviour of Alkylic Iodides with Alkylic Phosphites, or O-Phosphines. By C. A. AUGUST MICHAELIS and R. KAEHNE (*Ber.*, 1898, 31, 1048—1055).—The phenylic, parachlorophenylic, para- and meta-tolylic, and pseudocumenylic salts of phosphorous acid, $(OR_3)_3P$

(1 mol.), react with methylic iodide (1 mol.) at suitable temperatures, and also with benzylic chloride, yielding compounds, $(OR)_3PMeI$ or $(OR)_3PCl\cdot CH_2Ph$; with ethylic iodide, they would not combine in the same way; the products were often oils, but these sometimes solidified on cooling, or on washing with ether. They are decomposed by alkalis, and even by water, hydriodic acid, phenol, and an alkylic methyl- or benzyl-phosphinate being formed, $(OR)_3PMeI + H\cdot OH = HI + R\cdot OH + (OR)_2PMeO$. Ethylic phosphite will not combine with methylic iodide; instead of a normal compound, its decomposition products are obtained; one of these is *methylphosphinic acid*, for the preparation of which this reaction is convenient (see later.)

Triphenolmethyl-O-phosphonium iodide, $(OPh)_3PMeI$, prepared as indicated at 100°, melts at 70—75°, and is very deliquescent; *phenylic methylphosphinate*, $(OPh)_2PMeO$, melts at 36—37°. *Triphenolbenzyl-O-phosphonium chloride*, $(OPh)_3PCl\cdot CH_2Ph$, prepared at 175°, was not obtained pure; *phenylic benzylphosphinate*, $(OPh)_2PO\cdot CH_2Ph$, melts at 60°.

Parachlorophenylic phosphite (*parachlorophenol-O-phosphine*),

$$(C_6H_4Cl\cdot O)_3P,$$

boils at 290—297° under 15 mm. pressure. *Triparachlorophenolmethyl-phosphonium iodide*, $(C_6H_4Cl\cdot O)_3PMeI$, melts at 71°. *Parachlorophenylic methylphosphinate*, $(C_6H_4Cl\cdot O)_2PMeO$, boils at about 245° under 20 mm. pressure.

Paratolylic phosphite (*triparacresol-O-phosphine*), $(C_6H_4Me\cdot O)_3P$, from paracresol (3 mols.) and phosphorous chloride (1 mol.), boils at 250—255° under 10 mm. pressure. *Triparacresolmethyl-O-phosphonium iodide*, $(C_6H_4Me\cdot O)_3PMeI$, prepared at 100°, could not be obtained quite pure; *paratolylic methylphosphinate*, $(C_6H_4Me\cdot O)_2PMeO$, boils at 220—225° under 12 mm. pressure.

Metatolylic phosphite (*trimetacresol-O-phosphine*) boils at 235—238° under 7 mm. pressure, at 240—243 under 10 mm. *Trimetacresol-methyl-O-phosphonium iodide*, prepared at 100°, is very hygroscopic, and was not obtained pure; *metatoluic methylphosphinate* boils at 200—205° under 7 mm. pressure.

Pseudocumenylic phosphite (*pseudocumenol-O-phosphine*),

$$(C_6H_2Me_3\cdot O)_3P,$$

boils at 270—274° under 16 mm. pressure, and has a sp. gr. = 1·097 at 17°. The methylphosphonium iodide was not obtained solid. *Pseudocumenylic methylphosphinate*, $(C_6H_2Me_3\cdot O)_2PMeO$, melts at 79—90°.

When ethylic phosphite is heated with methylic iodide for 12 hours at 220°, an inflammable gas, presumably ethylene, is formed, and also ethylic iodide, and a solid product from which methylphosphinic acid, $PMeO(OH)_2$, can be isolated. This solid is dissolved in nitric acid, fuming nitric acid added, and the whole evaporated to dryness; the residue is then dissolved in water, and treated with excess of lead oxide made into a thin paste with water. From the mixture of lead salts formed, lead oxide and lead methylphosphinate are extracted with excess of acetic acid, lead phosphate remaining undissolved, the lead

in the filtrate is precipitated with hydrogen sulphide, and the filtrate freed from acetic acid by repeated evaporation with water, when the methylphosphinic acid is left as a white, crystalline mass, resembling spermaceti in appearance. C. F. B.

Action of Phosphorus Thiochloride on Solutions of Phenols in Aqueous Alkalis. By WILHELM AUTENRIETH and OTTO HILDEBRAND (*Ber.*, 1898, 31, 1094—1111. Compare this vol., i, 14).—When a solution of phenol in 15—20 per cent. aqueous soda is heated on the water bath with phosphoryl thiochloride, *triphenylic thiophosphate*, $PS(OPh)_3$, is formed and crystallises from alcohol in slender prisms melting at 53°. It is scarcely attacked by aqueous alkalis, but is readily hydrolysed by alcoholic soda, *diphenoxythiophosphoric acid*, $PS(OPh)_2 \cdot OH$, being produced. This substance is, moreover, always formed by the action of the thiochloride on an alkaline solution of phenol, both in the cold and on heating, and is also produced by the hydrolysis of diphenoxythiophosphoryl chloride with alcoholic soda; it is a yellowish oil which cannot be distilled, and readily dissolves in alkalis. The *sodium* salt crystallises in lustrous plates and is soluble in alcohol.

When phosphoryl thiochloride is added to a well cooled alkaline solution of phenol, two compounds are produced, which are the mono- and di-phenoxy-derivatives. *Diphenoxythiophosphoryl chloride*, $PS(OPh)_2Cl$, crystallises in forms resembling those of gypsum, and melts at 66–67°; it is stable towards water, hydrochloric acid, and aqueous alkalis, but is converted by alcoholic soda into diphenylthiophosphoric acid. The chloride is converted by aqueous ammonia into *diphenoxythiophosphamide*, $PS(OPh)_2 \cdot NH_2$, which crystallises in white, nacreous plates melting at 115°, and is sparingly soluble in hot water. *Diphenoxythiophosphanilide*, $PS(OPh)_2 \cdot NHPh$, formed by the action of aniline on the amide, crystallises in slender prisms melting at 92°. *Diphenoxythiophosphodiethylamide*, $PS(OPh)_2 \cdot NEt_2$, crystallises in lustrous prisms melting at 58°.

Phenoxythiophosphoryl dichloride, $OPh \cdot PSCl_2$, is a colourless liquid which can be distilled under diminished pressure. *Phenoxythiophosphodiamide*, $PS(OPh)(NH_2)_2$, crystallises in lustrous plates melting at 119°; *Phenoxythiophosphodianilide*, $OPh \cdot PS(NHPh)_2$, forms lustrous crystals melting at 126°, whilst the corresponding *phenylhydrazide*, $(OPh) \cdot PS(NH \cdot NHPh)_2$, crystallises in lustrous, slender needles melting at 136°.

Phenoxythiophosphamic acid, $OPh \cdot PS(NH_2) \cdot OH$, is prepared by heating the dichloride with aqueous ammonia, and crystallises in slender needles melting at 127—128°; when boiled with water, it yields ammonium phosphate, phenol and hydrogen sulphide. Alcoholic soda converts the dichloride into *phenoxythiophosphoric acid*, $OPh \cdot PS(OH)_2$, which has only been obtained as a syrup.

Paracresol readily reacts with phosphorus thiochloride, but the sole product of the reaction appears to be *diparatolyloxythiophosphoryl chloride*, $PS(O \cdot C_6H_4Me)_2Cl$, which melts at 53°, and closely resembles the corresponding phenyl derivative in its properties. *Diparatolyloxy-*

thiophosphamide, $PS(O\cdot C_6H_4Me)_2\cdot NH_2$, crystallises in lustrous plates melting at 131°, whilst the *anilide* crystallises in slender needles and melts at 106°.

Triparachlorophenylic thiophosphate, $PS(O\cdot C_6H_4Cl)_3$, crystallises in tablets and melts at 113—114°. *Diparachlorophenoxythiophosphoryl chloride*, $PS(O\cdot C_6H_4Cl)_2Cl$, melts at 92°, and when treated with ammonia yields the corresponding *amide*, which crystallises in lustrous plates melting at 96°.

β-Naphthol reacts very vigorously with the thiochloride, forming a mixture of the mono- and di-chlorides, which cannot be directly separated, but when treated with ammonia yields the corresponding amides, which can readily be obtained pure. *β-Naphthoxythiophosphodiamide*, $C_{10}H_7\cdot O\cdot PS(NH_2)_2$, crystallises in lustrous plates melting at 176°, whilst *β-naphthoxythiophosphamide*, $PS(OC_{10}H_7)_2\cdot NH_2$, separates from dilute alcohol in slender needles melting at 215°. A. H.

Iodinium Compounds Prepared by the Action of the Iodochlorides on Mercury Organic Compounds. By CONRAD WILLGERODT (*Ber.*, 1898, **31**, 915—922).—The iodochlorides react with mercurydiphenyl and phenylmercuric chloride to form double salts of the iodinium chlorides with mercuric chloride. *Diphenyliodinium mercurichloride*, $(Ph_2ICl)_2,HgCl_2$, which decomposes at 203°, is formed by the action of phenyliodochloride both on mercurydiphenyl and phenylmercuric chloride, and is also produced when solutions of diphenyliodinium chloride and mercuric chloride are mixed. Phenylmercuric chloride does not appear to form any similar double salt, and the author was unable to obtain the salt, $Ph_2ICl,HgCl_2$, described by Hartmann and Meyer (Abstr., 1894, i, 461). *Phenylorthotolyliodinium chloride*, $C_6H_4Me\cdot IPhCl$, crystallises in short prisms melting at 213—214°; the *platinochloride* in yellow needles, decomposing at about 191°; the *mercurichloride* in long, white needles melting at 135—137°, whilst the *dichromate* decomposes at 141—143°; the *iodide* crystallises in short, colourless prisms decomposing at 165°; the *nitrate* decomposes at 183—185°, and the *sulphate* at 171°. The corresponding *hydroxide*, $C_6H_4Me\cdot IPh\cdot OH$, has hitherto only been obtained in aqueous solution. *Phenylparatolyliodinium chloride* forms large, white prisms, melts at 208°, and is more readily soluble in water than the ortho-compound. The *platinochloride* decomposes at 195—198°; the *dichromate* explodes at 155—157° and the *iodide* decomposes at 170°, whilst the *mercurichloride* crystallises in matted plates, melting at 157°, and the *nitrate* in large plates melting at 138—140°. The hydroxide has only been obtained in the form of an amorphous, varnish-like mass. *Phenyl-β-naphthyliodinium chloride*, $C_{10}H_7\cdot IPhCl$, crystallises in short, acicular plates melting at 197°, and forms a *platinochloride* which decomposes at 171—173°, and an *iodide* which decomposes at 156—160°. The *hydroxide* forms a crystalline mass which has a strongly alkaline reaction. It was found impossible to obtain a phenylethyliodinium chloride by the action of an iodochloride on either mercury ethide or ethylmercurichloride, the products being ethylic chloride, iodobenzene, and ethylmercurichloride or mercuric chloride. A. H.

Acetals of Aldehydes and Ketones. By LUDWIG CLAISEN (*Ber.*, 1898, 31, 1010—1019. Compare E. Fischer and Giebe, this vol., i, 168).—Pursuing his discoveries regarding the formation of acetals of aldehydes, ketones, and ketonic acids by the agency of orthoformates (Abstr., 1896, i, 464; 1897, i, 188), the author has been led to replace the orthoformates by the hydrochlorides of imidoformates; these are known to yield orthoformates with alcohol at the ordinary temperature (Pinner, Abstr., 1883, 731), and they are now found to react with ketones, &c., in alcoholic solution, yielding acetals in accordance with the equation $CR_2O + 2EtOH + OEt\cdot CH{:}NH,HCl = CR_2(OEt)_2 + H\cdot COOEt + NH_4Cl$. The ketone (1 mol.) is mixed with alcohol (5 mols.), the mixture well cooled, and the imidoformate hydrochloride ($1\frac{1}{4}$ mols.) is gradually added, after which the whole is allowed to remain for several days, first in a refrigerator, then at the ordinary temperature. Plenty of ether is then added, the liquid is filtered from ammonium chloride, treated with ice and water containing a few drops of ammonia, and the ethereal layer removed and dried with potassium carbonate. The ether is next evaporated, and the residue fractionated under diminished pressure if the acetal have a high boiling point, otherwise under atmospheric pressure, in which case it is advisable first to let the liquid remain for some time with plenty of calcium chloride, in order that the alcohol may be removed as completely as possible. In some cases, no reaction occurs; for example, with benzophenone, although acetophenone does react, ethylic benzoylformate yields no acetal, although the pyruvate (acetylformate) does. Nor does camphor or carvole yield an acetal; the latter, in fact, gives + limonene. The yield is about the same as by E. Fischer's method in the case of aliphatic and of nitro- and chloro-aromatic aldehydes; those aldehydes which correspond with stronger acids seem to give a larger yield. In the case of other aromatic aldehydes, the new method is to be preferred, and it also yields acetals in the case of ketones, unlike the other method. By using methylic alcohol and methylic imidoformate, dimethylacetals can be obtained. The acetals obtained are enumerated below, together with such of their constants (boiling points and specific gravities at 15°) as have not been published before; when the name of the aldehyde, &c., is alone given, the *ethyl-acetal* only is described in the paper.

Acetaldehyde, œnanthaldehyde, acraldehyde, and crotonaldehyde do not yield the corresponding acetals, but compounds

$$OEt\cdot CH_2\cdot CH_2\cdot CH(OEt)_2$$

and $OEt\cdot CHMe\cdot CH_2\cdot CH(OEt)_2$, the latter of which boils at 73—74° under 14 mm. pressure. [The author prefers these formulæ to those, $OEt\cdot CHMe\cdot CH(OEt)_2$ and $OEt\cdot CHEt\cdot CH(OEt)_2$, proposed by Newbury (Abstr., 1891, 285)]. *αβ-Dibromopropaldehyde: dimethylacetal*, 108°, under 15 mm.; *diethylacetal*, 127—129°, under 22 mm.; the latter of these is converted by alcoholic potash into the *diethylacetals* of *monobromacraldehyde*, 181—183°, and *propiolaldehyde*, 140°. Furfuraldehyde: *diethylacetal*, 189—191°, sp. gr. = 1·0075. Benzaldehyde. *Cuminaldehyde: dimethylacetal*, 244—245°, sp. gr. = 1·0633; *diethylacetal*, 257—259°, sp. gr. = 0·9254. *Metanitrobenzaldehyde*: *dimethylacetal*, 162—164° under 19 mm., sp. gr. = 1·209; *diethylacetal*, 178°, under 21 mm., sp. gr. = 1·131. *Anisaldehyde*: dimethylacetal; *diethylacetal*, 261—263°; sp.

gr. = 0·9908. *Piperonaldehyde*: dimethylacetal, sp. gr. = 1·206; *diethylacetal*, 279—281° (153—154°, under 11 mm.), sp. gr. 1·129. *Cinnamaldehyde*; *dimethylacetal*, 125—127°, under 11 mm., sp. gr. = 1·023; *diethylacetal*, 264—266° (140—142°, under 12 mm.), sp. gr. = 0·981. *Monobromocinnamaldehyde*: *dimethylacetal*, 161—162°, under 15 mm., sp. gr. = 1·358; *diethylacetal*, 170—171°, under 15 mm., sp. gr. = 1·266; both of these yield *acetals* of *phenylpropiolaldehyde* when heated with alcoholic potash.

Acetone. *Acetophenone*: *dimethyl-*, *diethyl-* (212—216°, with some decomposition; compare following abstract), and *dipropyl-acetals*. *Ethylic pyruvate*: *diethylacetal*, 190—191°. [A fuller account of the acetals of ketones and ketonic acids is to be given in a later paper.]

Acetaldehyde diethylacetal (1 mol.), when heated with acetic anhydride (1 mol.) at 150° in a sealed tube, yields a *compound*, OAc·CHMe·OEt, boiling at 125—130°; sp. gr. = 0·941. In a similar way (except that further heating at 200° is necessary), benzaldehyde diethylacetal yields a compound OAc·CHPh·OEt, boiling at 243—245°. C. F. B.

Action of Agents which can remove the elements of Alcohol on some Acetals. By LUDWIG CLAISEN (*Ber.*, 1898, **31**, 1019—1021).—In the case of ethylic acetoacetate diethylacetal (Abstr., 1896, 464), it has been shown that distillation under atmospheric pressure can remove the elements of alcohol from an acetal, $CH_3 \cdot CR(OEt)_2$, forming a compound $CH_2 : CR(OEt)$. In general, however, this is not the case; some agent is necessary in order to remove the alcohol. Phosphoric anhydride may be used (as with ethylic pyruvate acetal), but it cannot be used alone in the case of acetals of aldehydes and ketones, for these, especially the latter, are very easily decomposed by acids. A mixture of phosphoric acid with a tertiary amine, such as pyridine or quinoline (ordinary acetal), may be used however; the base serves to neutralise the ethylphosphoric acid which is formed. In the case of acetals that more readily lose alcohol, the phosphoric anhydride may be replaced by an acid chloride; if the expected product have a low boiling point, quinoline and benzoic chloride should be used; if a high one, pyridine and acetic chloride (acetophenone acetal). A few compounds prepared by this method from acetals are enumerated below, with their boiling points; a more detailed account is to be published later.

Ethylic α-ethoxyacrylate, $CH_2 : C(OEt) \cdot COOEt$, 180°; hydrolysis converts it into *α-ethoxyacrylic acid*, which melts at 62°. [Merz and Otto's acid, melting at 110° (Abstr., 1890, 957), is possibly the β-ethoxy acid]. $CH_2 : CPh \cdot OEt$, 209—211°. $CH_2 : CMe \cdot OEt$, 59—62°;

$CH_2 : CMe \cdot OMe$, 38°.

Ethylic vinylic ether, $CH_2 : CH \cdot OEt$. C. F. B.

Propargylaldehyde [Propiolaldehyde] and Phenylpropargylaldehyde [Phenylpropiolaldehyde]. By LUDWIG CLAISEN (*Ber.*, 1898, **31**, 1021—1023).—The acetals of these aldehydes are prepared by heating the acetals of αβ-dibromopropaldehyde and α-bromocinnamaldehyde respectively with alcoholic potash; when heated with dilute sulphuric acid, they yield the aldehydes. These aldehydes are decomposed by aqueous soda in the cold, acetylene or phenylacetylene

being evolved and a formate formed; the action is in some respects analogous to that of alkalis on chloral.

Propiolaldehyde, CH⋮C·CHO, boils at 59—61°, and affects the nose and eyes even more than acraldehyde does. A crystalline anilide and hydrazone were prepared. The *dimethylacetal* boils at 110°, the *diethylacetal* at 139—141°; the latter forms a feebly explosive silver derivative, CAg⋮C·CH(OEt)$_2$.

Phenylpropiolaldehyde, CPh⋮C·CHO, which boils at 118° under 17 mm. pressure, decomposes and gives off carbonic oxide when distilled under atmospheric pressure. The anilide, hydrazone, phenylhydrazone, semicarbazone, and hydrocyanide were prepared, and also condensation products with acetone, acetophenone, and malonic acid. The *diethylacetal* boils at 148° under 14 mm. pressure. C. F. B.

Normal Octyl Compounds. By PAUL LIPINSKI (*Ber.*, 1898, **31**, 938—942).—*Octylphenyl methyl ketone*, $C_8H_{17}\cdot C_6H_4\cdot COMe$, formed by the action of acetic chloride on octylbenzene in the presence of aluminium chloride, is a yellowish oil with a faint aromatic odour. The *oxime* crystallises in white plates melting at 42—43°. *Octylphenyl phenyl ketone*, $C_8H_{17}\cdot C_6H_4\cdot COPh$, is a yellowish-brown oil which boils at 104—110° under a pressure of 85 mm., and yields an *oxime* melting at 106—107°. *Octylphenylazo-α-naphthol*, $C_8H_{17}\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, crystallises from alcohol in red plates, which are prepared by nitrating octylbenzene, reducing, and treating the solution of the product of reduction with nitrous acid and α-naphthol. *Paramethyloctylbenzene* (para-octyltoluene) melts at 11—12°, boils at 281—283°, and is converted by oxidation into terephthalic acid. *Para-octyltoluenesulphonic* [*paramethyloctylsulphonic*] *acid*, obtained by shaking paramethyloctylbenzene with fuming sulphuric acid, forms white, deliquescent crystals. The salts of *barium* and *lead* are soluble in water and crystallise well. *Mononitroparamethyloctylbenzene*, $C_8H_{17}\cdot C_6H_3Me\cdot NO_2$, which is produced, along with the dinitro-compound, by the action of fuming nitric acid on paramethyloctylbenzene, melts at 19—20°, forming a yellowish oil which cannot be distilled. The *dinitro*-compound is also an oil which cannot be distilled. *Paramethyloctylphenyl methyl ketone*, $C_8H_{17}C_6H_4Me\cdot COMe$, is a yellowish liquid which has not been further examined. A. H.

A New Method of Preparing Acid Cyanides. By LUDWIG CLAISEN (*Ber.*, 1898, **31**, 1023—1024).—When pyridine is added slowly to an ethereal solution of benzoic chloride and anhydrous hydrogen cyanide, benzoic cyanide is obtained, together with some dibenzoic dicyanide: $C_6H_5\cdot COCl + HCN + C_5NH_5 = C_6H_5\cdot CO\cdot CN + C_5NH_5,HCl$. The reaction is probably a general one, and affords a convenient means of preparing acid cyanides. If the acid chloride be added to a mixture of hydrogen cyanide with pyridine, the polymeric cyanide is almost the only product. C. F. B.

Paraxylylacetic Acid. By GUERBET (*Compt. rend.*, 1897, **125**, 34—37).—A good yield of Claus' paraxylyl methyl ketone can only be obtained under the following conditions. Aluminium chloride (20 grams), placed in a reflux apparatus, is covered with dry

carbon bisulphide, the flask is heated to 50°, and a mixture of acetic chloride (75 grams) and paraxylene (100 grams) gradually added from a dropping funnel, a further quantity of aluminium chloride (40 grams) being finally added. The operation takes about half an hour, and the mixture is then poured on to ice.

Paraxylylacetamide, obtained when the ketone (5 grams), 95 per cent. alcohol (4 grams), ammonium hydrosulphide (15 grams), and sulphur (2 grams) are heated for 48 hours at 200°, crystallises from alcohol in large, colourless needles melting at 154°. When hydrolysed by boiling with alcoholic potash (33 per cent.) for 8 days, it yields *paraxylylacetic acid*, $C_6H_3Me_2\cdot CH_2\cdot COOH$, which crystallises from 60 per cent. alcohol in colourless, prismatic needles melting at 128°. The *potassium* salt is extremely deliquescent; the *sodium* salt crystallises with $1H_2O$, the *calcium* salt with $3H_2O$; the *barium* salt is anhydrous and much more soluble than the calcium salt. The *methylic* salt boils at 253—254°, and the *ethylic* salt at 261·5°.

When oxidised with potassium permanganate, the acid yields unsymmetrical trimesic acid. J. J. S.

Tautomerides. By ROBERT SCHIFF (*Ber.*, 1898, **31**, 1388—1395. Compare this vol., i, 237).—The author has shown that sodium ethoxide converts the ketonic modification of ethylic benzylidenediacetoacetate into the enolic form, which develops an intense coloration with ferric chloride, whilst piperidine exerts the converse influence.

When ethylic ethylidenediacetoacetate (Knoevenagel, Abstr., 1895, i, 51), is prepared from ethylic acetoacetate (2 mols.) and acetaldehyde (1 mol.) in presence of piperidine, the ketonic form crystallises from the liquid, and develops no coloration with ferric chloride; when the alcoholic solution is boiled, however, the enolic isomeride is generated. In order to prepare the latter, the ketonic salt is mixed with cold alcoholic sodium ethoxide (2 mols.), and, in presence of ice, treated with the corresponding amount of dilute hydrochloric acid; lustrous needles separate, developing a deep violet coloration with ferric chloride, but this property is gradually lost when the crystals are exposed to air, until, when quite dry, the substance is indifferent towards the agent, and melts at 78—79°.

Benzylideneaniline is a convenient agent for fixing tautomeric forms; in fact, all analogous condensation products of aromatic bases and aldehydes, excepting salicylaldehyde, appear suitable for this purpose.

Enolic ethylic benzylidene-β-naphthylamidoacetoacetate,

$$OH\cdot CMe{:}C(COOEt)\cdot CHPh\cdot NH\cdot C_{10}H_7,$$

is prepared by adding finely divided benzylidene-β-naphthylamine to the enolic modification of ethylic acetoacetate (Kahlbaum); it dissolves in a small proportion of warm benzene, and separates as a white, crystalline precipitate on adding petroleum to the cold solution. It melts at 100—101°. The *ketonic* compound,

$$COMe\cdot CH(COOEt)\cdot CHPh\cdot NH\cdot C_{10}H_7,$$

is obtained from common specimens of ethylic acetoacetate by adding benzylidene-β-naphthylamine, and a small quantity of piperidine; it

melts at 74—75°, and yields ethylic phenylcarbinolacetoacetate (*loc. cit.*) under the influence of sodium ethoxide.

Ketonic ethylic dianilidobenzylideneacetonedicarboxylate,

$$CO[CH(COOEt)\cdot CHPh\cdot NHPh]_2,$$

is obtained on adding a few drops of piperidine to mixed solutions of ethylic acetonedicarboxylate and benzylideneaniline (2 mols.) in benzene; it melts at 117—118°, and gives no coloration with ferric chloride. When piperidine is not employed, a mixture of the ethereal salt and benzylideneaniline (2 mols.) yields, after some hours, a white, insoluble compound which melts at 134°, and is isomeric with the foregoing substance; the authors regard it as a mixture form of the tautomeric modifications. The *enolic* compound,

$$NHPh\cdot CHPh\cdot CH(COOEt)\cdot C(OH):C(COOEt)\cdot CHPh\cdot NHPh,$$

is produced on mixing benzene solutions of ethylic acetonedicarboxylate and benzylideneaniline in molecular proportion; the white, microcrystalline substance is washed with light petroleum and benzene, and melts at 139°.

Ethylic benzylidenediacetonedicarboxylate,

$$CHPh[CH(COOEt)\cdot CO\cdot CH_2\cdot COOEt]_2,$$

prepared by adding 2 vols. of alcohol and a small quantity of piperidine to a mixture of benzaldehyde and ethylic acetonedicarboxylate (2 mols.), melts at 130°, and is in part resolved into its components under the influence of boiling alcohol.

Ketonic anilidobenzylideneacetylacetone,

$$COMe\cdot CH(COMe)\cdot CHPh\cdot NHPh,$$

is obtained on adding a small quantity of piperidine to a mixture of benzylideneaniline and acetylacetone in molecular proportion; it separates when petroleum is added to its benzene solution, and melts at 83—84°. The substance develops a feeble red coloration with ethereal ferric chloride. The *compound* obtained without the influence of piperidine is the isomeric mixture form, and melts at 103°; it develops an intense red coloration with ferric chloride. The *enolic* compound, $OH\cdot CMe:C(COMe)\cdot CHPh\cdot NHPh$, is formed in presence of a small quantity of dry sodium ethoxide; it crystallises from benzene on the addition of petroleum, in lustrous, white needles and melts at 109°. A deep red coloration with ferric chloride reveals the hydroxylic character of this modification.

Benzylidenediacetylacetone (Knoevenagel, *loc. cit.*), resembles ethylic benzylidenediacetoacetate and ethylic ethylidenediacetoacetate in chemical behaviour; the ketonic form melts at 167—168°, and is indifferent towards ferric chloride.

Ketonic anilidobenzylidenebenzoylacetone,

$$COMe\cdot CH(COPh)\cdot CHPh\cdot NHPh,$$

cannot be crystallised owing to its insoluble character; it melts at 172—173°, and is probably a polymeride. The *enolic* compound, $OH\cdot CMe:C(COPh)\cdot CHPh\cdot NHPh$, crystallises very slowly from petroleum, and melts at 83—84°; it develops an intense dark red coloration with ferric chloride.

M. O. F.

Ethylic Anisoylacetoacetate and its Derivatives. By ALBERT SCHOONJANS (*Chem. Centr.*, 1897, ii, 616; from *Bull. Acad. roy. Belg.*, [iii], 33, 810—820).—A yield of 110 per cent. of anisic chloride is

obtained from anisic acid by heating the dry acid (1 mol.) with phosphorus pentachloride (1 mol.), then removing the phosphorus oxychloride by means of a current of dry air, and distilling the residue on a L. Meyer's air bath. *Anisic chloride* is a colourless, highly refractive liquid, boils at 160—164° under a pressure of 35 mm., at 152—153° under 24 mm., and at 145° under 14 mm.; when mixed with cold water and cooled, it forms matted needles which melt at 22°. *Ethylic anisoylacetoacetate*, prepared like the benzoylacetoacetate, forms an oily liquid which decomposes when distilled in a vacuum. With copper acetate, its alcoholic solution forms the compound $Cu(C_{14}H_{15}O_5)_2$, which crystallises from hot alcohol in small tablets, and from chloroform, in which it is very soluble, in small, lustrous needles. When ethylic anisoylacetoacetate is shaken with twice its weight of 10 per cent. ammonia, a yellow precipitate forms which dissolves on warming, and then *ethylic anisoylacetate* separates as a colourless oil of pleasant odour; this oil is insoluble in water, but miscible with alcohol and ether, boils at 140—142° under a pressure of 10 mm., has a sp. gr. = 1·0338 at 19°, gives a deep red coloration with ferric chloride in alcoholic solution, and with copper acetate an olive-green substance, $Cu(C_{12}H_{13}O_4)_2$, which crystallises from alcohol or chloroform in small needles, and decomposes at 180°. By the action of hydroxylamine hydrochloride in glacial acetic acid on ethylic anisoylacetate, a substance, which is probably *anisylisoxazolone*, is formed; it crystallises from hot alcohol in long, yellow needles, melts and decomposes at 143°, is slightly soluble in light petroleum, easily soluble in hot benzene, and soluble in cold alkalis; with ferric chloride in alcoholic solution, it forms an inky-black liquid, reduces ammoniacal silver solutions, and is easily decomposed by alcoholic potassium hydroxide in the cold. *Dehydroanisoylacetic acid*,

$$CO{<}\begin{matrix}CH(CO{\cdot}C_6H_4{\cdot}OMe){\cdot}CO\\ CH{:}C(C_6H_4{\cdot}OMe){\cdot}O\end{matrix},$$

is obtained from the brown mass which remains after rectifying the ethylic anisoylacetate, by washing with ether and crystallising from hot chloroform and alcohol. It crystallises in very light, golden-yellow, iridescent leaflets, is easily soluble in chloroform, slightly so in hot alcohol, but insoluble in the other usual solvents; with concentrated sulphuric acid, it gives a yellowish-red solution, which, on heating, becomes brown with a green fluorescence, and finally colourless; with ferric chloride in alcoholic solution, it gives a purple-red coloration. It dissolves in cold ammonia, and the solution, when evaporated, yields the unchanged substance. When the ammoniacal solution is neutralised with nitric acid and silver nitrate added, a yellow precipitate, which is soluble in ammonia and not affected by light, is obtained. E. W. W.

Amides of two substituted Orthoaldehydo-acids. By AUGUSTIN BISTRZYCKI and ENRIQUE FYNN (*Ber.*, 1898, 31, 922—929).—The substance obtained by the action of phosphorus pentachloride on bromopianic acid, which was described by Tust (Abstr., 1892, 1209) as a trichloride, $COCl{\cdot}C_6HBr(OMe)_2{\cdot}CHCl_2$, is in reality the monochloride, $COCl{\cdot}C_6HBr(OMe)_2{\cdot}CHO$, and melts at 98—99°. On treatment with ammonia, it yields the amide, which, after crystallisation from chloro-

form, melts at 200°, whilst Tust gives 180° as the melting point after recrystallisation from water. The amide readily reacts with hydroxylamine hydrochloride, two products being formed. The first of these has the composition of the normal oxime, and crystallises in needles which melt and decompose at 267°; when heated with acetic anhydride, however, it simply yields an *acetyl* derivative, melting at 242°, and not bromopiazone, $C_6HBr(OMe)_2<\begin{matrix}CO\cdot NH\\ CH:N\end{matrix}$, as might have been expected; it seems probable, therefore, that this compound is not, in reality, a simple oxime. The second *product*, $C_{10}H_8NBrO_5$, crystallises in fascicular groups of needles melting at 227°, and is an oxidation product; it yields an *acetyl* derivative, which crystallises in tablets and melts at 159°. *Bromopiazone*, which is readily obtained by the action of hydrazine sulphate on bromopianic acid, crystallises in colourless, matted needles melting at 231—232°; its *acetyl* derivative also forms colourless needles melting at 173°. Bromopianic amide itself does not yield an anhydride when it is treated with acetic anhydride, but is converted into a *diacetyl* derivative, $C_{10}H_8BrNO_4Ac_2$, which crystallises in needles melting at 150°.

Nitro-opianic chloride, $NO_2\cdot C_6H(OMe)_2(CHO)\cdot COCl$, forms faintly yellow, lustrous plates melting at 137—138°. The corresponding *amide* crystallises in yellow, lustrous needles, which melt and decompose at 203°; this compound behaves towards hydroxylamine in a precisely similar manner to the bromopianic amide, and the *compound* produced crystallises in yellow needles which melt and decompose at 265°, whilst the *acetyl* derivative crystallises in tablets, and decomposes at 246°.

A. H.

Condensation Products from the Amides of two Orthoaldehydo-acids. By AUGUSTIN BISTRZYCKI and EDWARD FINK (*Ber.*, 1898, 31, 930—936. Compare the foregoing abstract).—Bromopianic amide is converted by phosphorus oxychloride into *bisbromometa-opindolone*, $C_6HBr(OMe)_2<\begin{matrix}CO\cdot N—N\cdot CO\\ CH\cdot CH\end{matrix}>C_6HBr(OMe)_2$, which forms a very sparingly soluble, brownish powder, and can be heated to 325° without undergoing any change. By reduction with tin and hydrochloric acid, it is converted into *dihydrobisbromometa-opindolone*, $C_{20}H_{18}N_2Br_2O_6$, a white, amorphous mass, and *bromohemipinic isoimidine*, $C_6HBr(OMe)_2<\begin{matrix}C(OH)\\ CH_2\end{matrix}>N$, which crystallises in white needles melting at 203°; this compound yields an *acetyl* derivative, $C_{12}H_{12}NBrO_4$, which crystallises in small, white needles melting at 177—178°.

Bisnitrometa-opindolone, $(C_{10}H_8N_2O_5)_2$, is prepared in a similar manner to the bromo-derivative, which it closely resembles in properties. On reduction, it yields *amidohemipinic isoimidine*,

$$NH_2\cdot C_6H(OMe)_2<\begin{matrix}C(OH)\\ CH_2\end{matrix}>N,$$

the hydrochloride of which forms small, white needles; the free *base* crystallises in small prisms melting and decomposing at 223—224°, whilst the *diacetyl* derivative crystallises in white needles and decomposes at 242°. Amidohemipinic isoimidine can readily be converted

into the bromo-compound described above by means of the diazo-reaction, and this proves that, in bromopianic acid, the bromine atom occupies the same position in the ring as the nitro-group of nitro-opianic acid, which is known to have the constitution [$COOH : CHO : (OMe)_2 : Br = 1 : 2 : 5 : 6 : 3$]. A. H.

Derivatives of Orthosulphobenzoic Anhydride. By MICHAEL DRUCK SOHON (*Amer. Chem. J.*, 1898, 20, 257—278).—Orthosulphobenzoic anhydride, obtained by the action of phosphorus pentachloride on the acid potassium salt or by distilling the acid with phosphoric anhydride, forms clear, colourless, monoclinic, deliquescent crystals, melts at 129·5°, sublimes at or below its melting point, and can be distilled. Alcohols dissolve it with formation of the acid salts of orthosulphobenzoic acid. The *methylic* and *ethylic* hydrogen salts, and also their *silver* and *potassium* salts, are described.

Phenols act on the anhydride at a temperature of 130—135° with the production of sulphonphthaleins, which decompose on heating to a slightly higher temperature (about 150°) with evolution of hydrogen sulphide and formation of darker and less soluble products, which were not further investigated. No evidence of the formation of benzoylbenzenesulphonic acids could be obtained. The sulphonphthaleins are intensely coloured substances, more soluble in water than the corresponding derivatives of phthalic acid, and soluble in alcohol, from which they can be obtained crystalline by precipitation with ether.

Phenolsulphonphthalein, $SO_2<\substack{C_6H_4 \\ O}>C(C_6H_4 \cdot OH)_2$, is precipitated as a bright red, crystalline powder, but on slow evaporation of a glacial acetic acid solution, it separates in distinct nodules of radiating needles, appearing blue-green by reflected and deep red by transmitted light; it is about as sensitive to acids and alkalis as phenolphthalein, the colour of the alkaline solution varying from red to purple. When treated with zinc dust in alkaline solution, small, granular crystals of *phenolsulphonphthalin* are formed, and with bromine in glacial acetic acid solution, it yields *dibromophenolsulphonphthalein* as a granular, purplish, crystalline powder. It gives a yellow solution with acids, and a blue to purple coloration with alkalis; it is extremely delicate as an indicator, being sensitive to ammonia but not to carbonic anhydride.

Phenolsulphonphthalein does not give an acetyl derivative, and when fused with potash is converted into a sulphite, phenol, and paradihydroxybenzophenone.

Orthocresolsulphonphthalein, $C_{21}H_{18}SO_5$, separates from water in crystals, appearing bottle-green by reflected and deep carmine by transmitted light; its neutral or slightly acid solution is yellow, but with alkalis it gives a purple to carmine colour. With bromine, it forms a *dibromo*-derivative, and it can be acetylated.

Paracresolsulphonphthalein was not obtained pure; it has a yellow colour, and is somewhat fluorescent.

Resorcinolsulphonphthalein, $SO_2<\substack{C_6H_4 \\ O}>C<\substack{C_6H_3(OH) \\ C_6H_3(OH)}>O$, is a

bright reddish-yellow powder, intensely fluorescent in alkaline solution. The bromine derivative is not as intense in colour as eosin.

Orcinolsulphonphthalein is easily produced, and has been already described by Gilpin (*Amer. Chem. J.*, **16**, 528).

Quinolsulphonphthalein was obtained as a dark-brown mass, *pyrogallolsulphonphthalein* (*sulphongallein*) as a bluish-brown powder, *meta-amidophenolsulphonphthalein* as a reddish-brown powder, and the corresponding *para*-compound as a dark-coloured mass. Salicylic acid, when melted with the anhydride, gives a bright red colouring matter.

Ammonium benzaminesulphonate, obtained by the action of ammonia on the anhydride, crystallises from alcohol in needles melting at 256—257°. The corresponding *barium* and *potassium* salts are also described.

A similar reaction is given with aniline and the toluidines, with production of a salt of the base with a benzanilido-acid. The free acids are exceedingly soluble, and could not be obtained in a crystalline form, but the salts crystallise slowly from concentrated solutions. They are decomposed by boiling with acids or alkalis, yielding the base and orthosulphobenzoic acid, and with phosphorus pentachloride the corresponding sulphinide derivative is obtained.

Aniline benzanilidosulphonate separates from alcohol in white tufts of radiating needles. The *barium*, *ammonium*, *potassium*, *cadmium*, *sodium*, *copper*, *silver*, and *lead* salts are also described, from the last of which the *free acid* was obtained as a syrup by means of hydrogen sulphide.

Paratoluidine benzoparatoluido-orthosulphonate forms clusters of short, sharply-pointed needles, and the corresponding *orthotoluidine*-derivative, nodules of radiating needles. The *barium* and *potassium* salts are described.

The anhydride acts on acetamide and benzamide as a dehydrating agent, giving rise to the corresponding nitrile and orthosulphobenzoic acid; and with phosphorus pentachloride produces both chlorides of orthosulphobenzoic acid, excess of the reagent, continued action, and high temperature favouring the formation of the unsymmetrical chloride. A. W. C.

Paramethoxyorthosulphobenzoic Acid. By P. R. MOALE (*Amer. Chem. J.*, 1898, **20**, 288—298).—*Paramethoxyorthosulphobenzoic acid*, $COOH\cdot C_6H_3(OMe)\cdot SO_3H + 2\frac{1}{2}H_2O$, prepared from paratoluidineorthosulphonic acid according to the directions of Parks (Abstr., 1893, i, 585), crystallises from water in long, transparent, colourless needles melting at 104°. When heated in a test-tube to 145°, it lost water, and fine needles sublimed, but could not be obtained in sufficient amount for analysis. The *potassium*, *calcium*, *magnesium*, and *lead* salts are described.

When heated together with resorcinol, *paramethoxysulphonefluorescein* is obtained as a reddish, granular mass which dissolves in alkalis with a beautiful, reddish-green fluorescence; neither this nor the corresponding *orcinol* compound could be obtained quite pure. With phenol, a dirty-brown mass is formed, with which it was found impossible to deal satisfactorily. A. W. C.

Decomposition of Paradiazo-orthotoluenesulphonic Acid with Absolute Methylic Alcohol in presence of other Substances. By P. R. Moale (*Amer. Chem. J.*, 1898, **20**, 298—302).—When paradiazo-orthotoluenesulphonic acid is acted on with sodium methoxide in methylic alcohol solution, and the product treated respectively with phosphorus pentachloride and ammonia, orthotoluenesulphonamide is obtained in small amount, showing that the alkali causes the "hydrogen reaction" to take place to some extent. The residue is a black, tarry mass with which nothing could be done.

No definite results were arrived at when the decomposition was carried out with sodium ethoxide or caustic potash in ethylic alcohol solution, but by the action of dry ammonia gas in absolute methylic alcohol solution, and subsequent treatment of the residue with phosphorus pentachloride and ammonia, the amide of paratoluidine-orthosulphonic acid was obtained.

With aniline and methylic alcohol, three reactions take place according to the proportions of the reacting substances, one common product, and apparently three or four dyes, being formed. A. W. C.

Silver Paraphenolsulphonate. By Francesco Zanardi (*Chem. Centr.*, 1897, ii, 547; from *Boll. Chim. Farm.*, **36**, 449—452).—Paraphenolsulphonic acid is obtained as a thick syrup by decomposing barium paraphenolsulphonate with the calculated quantity of sulphuric acid. The aqueous solution of the acid, when treated with silver carbonate and evaporated at 20—25°, yields slender, white, prismatic needles of the silver salt; this is odourless, dissolves in 3 parts of water and in 80 parts of alcohol, and is insoluble in ether, chloroform, and carbon bisulphide; it is acted on by light, decomposes at 120°, and might be used as a disinfectant. E. W. W.

Parabenzoyldiphenylsulphone. By Lyman C. Newell (*Amer. Chem. J.*, 1898, **20**, 302—318).—Paratolylphenylsulphone prepared from paratoluenesulphonic chloride by Friedel and Craft's reaction, forms hexagonal plates melting at 124—125°. When oxidised with chromic acid in glacial acetic acid solution, it yields *paraphenylsulphonebenzoic acid*, crystallising from alcohol in small, white prisms melting at 273° (uncorr.), and not at above 300° as stated by Michael and Adair (Abstr., 1878, 415). The *calcium*, *barium*, and *sodium* salts are described. The free acid and its salts are readily acted on by phosphorus pentachloride yielding *paraphenylsulphonebenzoic chloride*, $SO_2Ph\cdot C_6H_4\cdot COCl$, which forms glistening, white plates, or short, white needles melting at 145·2—145·8°, and this substance, when treated with excess of concentrated ammonium hydroxide, is converted into *paraphenylsulphonebenzamide*, separating from alcohol in small transparent, acicular crystals melting at 242—243° (uncorr.); and with aniline it yields *paraphenylsulphonebenzanilide*, crystallising from alcohol in transparent, small prisms melting at 202—203° (uncorr.). *Parabenzoyldiphenylsulphone*, $SO_2Ph\cdot C_6H_4\cdot COPh$, prepared from the chloride by the action of benzene in presence of aluminium chloride, crystallises from alcohol in fine, white, lustrous needles, which, when dry, pack together like felt, and melt at 133° (uncorr.). It may be recovered unchanged from its solution in warm, concentrated nitric acid,

or cold, concentrated sulphuric acid, and is not attacked by boiling alcoholic potash. On fusion with potash, it does not decompose into benzoic acid and diphenylsulphone like the corresponding ortho-compound (compare Remsen and Saunders, Abstr., 1895, i, 474), but the exact nature of the decomposition products could not be determined.

On treatment with phenylhydrazine, the sulphone yields a *phenylhydrazone*, $NHPh\cdot N{:}CPh\cdot C_6H_4\cdot SO_2Ph$, separating from alcohol in lustrous, lemon-yellow needles melting at 184°, and also a small amount of a substance, which appears to be acetophenylhydrazide. The formation of this substance can only be explained by supposing that the alcohol used in the experiment may have been oxidised to acetic acid, which may then have united with the excess of phenylhydrazine present. The corresponding *oxime* crystallises from alcohol in irregular leaflets melting at 201°.

The author has confirmed the work of Remsen and Saunders, who failed to obtain either an oxime or a phenylhydrazone from orthobenzoyldiphenylsulphone. A. W. C.

Action of Phenyl- and Tolyl-hydroxylamines on Aromatic Thionylamines. By AUGUST MICHAELIS and KARL PETOU (*Ber.*, 1898, 31, 984—997).—A benzene solution of thionylaniline reacts with phenylhydroxylamine, yielding azobenzene and aniline phenylsulphonamate. Other thionylamines and β-substituted hydroxylamines react in a similar manner, 2 molecules of the former always reacting with 4 molecules of the latter. The reaction is a little more complex when the thionylamine and hydroxylamine contain different radicles, for example, $R\cdot N{:}SO$ and $R'NH\cdot OH$. When R and R′ are similar, then the azo-compound is formed merely from the hydroxylamine, and has the symmetrical formula $R'\cdot N{:}N\cdot R'$, a mixed sulphonamate, $R\cdot NH\cdot SO_3NH_3R'$, being formed at the same time. An exception to this is found in the reaction between parathionyltoluidine and phenylhydroxylamine, when the mixed azo-compound, benzeneazotoluene, is formed.

When the two radicles, R and R′, are very different, then a mixed azo-compound is always formed, for example, when xylyl-, ψ-cumyl- or naphthyl-thionylamines react with phenyl- or tolyl-hydroxylamines. These mixed azo-compounds are often red liquids, which can be purified by distillation in steam. In only one case, namely, by the action of paratolylhydroxylamine on metathionyltoluidine, was it found that the azo-compound was formed from the thionylamine, and had the symmetrical structure $R\cdot N{:}N\cdot R$, whilst a simple sulphonamate (2 mols.), $R'\cdot NH\cdot SO_3\cdot NH_3R'$, was formed at the same time.

A solution of phenylhydroxylamine (4 grams) in dry benzene (100 grams) readily reacts with thionylaniline (2·78 grams) also dissolved in benzene; after several hours, a crystalline mass of Wagner's aniline phenylsulphonamate (Abstr., 1886, 708) separates, and azobenzene remains dissolved in the benzene. Similarly, paratolylhydroxylamine (2 mols.) and thionylaniline (1 mol.) yield *paratoluidine phenylsulphonamate*, crystallising in white plates and melting at 236°, and an orange-yellow, crystalline azo-compound melting at 68—72°, probably orthotolueneazoparatoluene. Thionylaniline and orthotolylhydroxylamine

yield azo-orthotoluene and *orthotoluidine phenylsulphonamate*, which melts at 205° giving a bluish-purple liquid.

Thionylaniline and metatolylhydroxylamine yield *metatoluidine phenylsulphonamate*, which carbonises at 250°, and Jacobson's benzene azometatoluene (Abstr., 1896, i, 96).

Phenylhydroxylamine and parathionyltoluidine yield a mixture of sulphonamates melting at 223°, and benzeneazoparatoluene melting at 70—71°. Schultz (Abstr., 1884, 903), has previously described this compound as melting at 63°. Paratolylhydroxylamine and parathionyltoluidine yield parazotoluene and *paratoluidine paratolylsulphonamate* melting at 210—211°. [In other parts of the paper this is stated to melt at 235—236°]. Orthotolylhydroxylamine and parathionyltoluidine yield *orthotoluidine paratolylsulphonamate* melting at 228°, and *orthoazoxytoluene*, $(C_7H_7)_2N_2O$, which crystallises from alcohol in yellow needles melting at 59°. Metatolylhydroxylamine and parathionyltoluidine yield *metatoluidine paratolylsulphonamate* melting at 225—226°, and metazotoluene melting at 54—55°. Orthothionyltoluidine and phenylhydroxylamine yield a mixture of sulphonamates melting at 238—239°, and Jacobson's benzeneazo-orthotoluene. Orthothionyltoluidine and paratolyldroxylamine give *paratoluidine orthotolylsulphonamate*, melting at 241°, and parazotoluene.

The same thionyl compound reacts with orthotolylhydroxylamine, yielding *orthotoluidine orthotolylsulphonamate*, melting at 212°, and orthoazotoluene, and with metatolylhydroxylamine yielding *metatoluidine orthotolylsulphonamate*, melting at 208°, and metazotoluene. Metathionyltoluidine and phenylhydroxylamine yield a mixture of sulphonamates and benzeneazometatoluene. The same thionyl compound reacts with paratolylhydroxylamine, yielding *paratoluidine paratolylsulphonamate*, melting at 235—236°, and metazotoluene. This is the only instance in which it has been found that the azo-compound is derived solely from the thionylamine. Metathionyltoluidine and orthotolylhydroxylamine yield a mixture of sulphonamates, melting at 219°, and Schultz's metatoluene-azo-orthotoluene. The same thionylamine and metatolylhydroxylamine yield *metatoluidine metatolylsulphonamate*, melting at 202°, and metazotoluene. Thionylmetaxylidine reacts with phenyldroxylamine, yielding a mixture of sulphonamates and benzeneazometaxylene; the latter is a red oil and is identical with the compound obtained by the action of nitrosobenzene on unsymmetrical metaxylidine.

Paratolueneazometaxylene is obtained by the interaction of asymmetrical metathionylxylidine and paratolylhydroxylamine; when purified by distillation in steam and recrytallisation from alcohol, it forms yellowish-red, flat needles melting at 62°.

Thionylpseudocumidine reacts with phenylhydroxylamine, yielding a mixture of sulphonamates, melting at 218°, and *benzeneazopseudocumene*, which is a red oil. *Paratolueneazopseudocumene* crystallises in yellow needles melting at 58°. Benzeneazo-α-naphthalene, obtained from thionyl-α-naphthylamine and phenylhydroxylamine, crystallises from alcohol in small brick-red crystals melting at 70°; Nietzki and Zehntner (Abstr., 1893, i, 275) give the melting point as 63·5°. *Metatoluene-azo-α-naphthalene* melts at 43—44°.

Phenylhydroxylamine and thionyl-paraphenylenediamine react better in chloroform than in benzene solution; a crystalline sulphonamate, consisting probably of a mixture of aniline phenylsulphonamate and aniline paraphenylenedisulphonamate, is deposited, which carbonises between 200° and 300° without melting. The chloroform solution contains the *triazo*-compound, $PhN_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N_2Ph$, which, after recrystallisation from alcohol and sublimation, forms orange-red needles; it melts at 166—167°, and, when carefully heated, sublimes. Paratolylhydroxylamine, when treated in a similar manner, yields the *triazo*-compound, $N_2(C_6H_4 \cdot N_2 \cdot C_6H_4Me)_2$, melting at 201—202°. Both these compounds are sparingly soluble in alcohol or ether, somewhat more soluble in benzene, and readily soluble in chloroform. J. J. S.

Oxidation of Paranitrotoluenesulphonic Acid. By ARTHUR G. GREEN and ANDRÉ R. WAHL (*Ber.*, 1898, **31**, 1078—1080. Compare this vol., i, 200).—In reply to the criticism of Ris and Simon (this vol., i, 322), the authors point out that the compound described by them as dinitrodibenzyldisulphonic acid was in reality the free acid and not the sodium hydrogen salt as maintained by Ris and Simon. When a solution of normal sodium dinitrodibenzylsulphonate is acidified, the nature of the product depends on the conditions. Strong solutions yield the monosodium salt, dilute solutions the free acid. Solutions of intermediate strength yield the monosodium salt when slowly cooled, but when the liquid is quickly cooled, the free acid separates in plates which are converted into the monosodium salt by prolonged contact with the mother liquor. The authors also maintain the accuracy of their formula, $C_{14}H_{10}N_2S_2O_{10}$, for the dinitrostilbenesulphonic acid, as against the formula, $C_{14}H_{10}N_2S_2O_9$, proposed by Ris and Simon, and have further confirmed it by a quantitative reduction experiment, carried out with a weighed amount of zinc dust, the excess of zinc being afterwards estimated by Wahl's method (this vol., ii, 190). A. H.

Reduction of Aromatic Ketones by Sodium and Alcohol. By AUGUST KLAGES and PAUL ALLENDORFF (*Ber.*, 1898, **31**, 998—1010). —Purely aromatic ketones, CRR′O, are reduced by sodium in boiling ethyl alcoholic solution to methane derivatives, CH_2RR'. Mixed aliphatic-aromatic ketones, $CH_3 \cdot CRO$, are only reduced to carbinols, $CH_3 \cdot CHR \cdot OH$; a little of the melthane derivative, $CH_3 \cdot CH_2R$, is indeed obtained, but this is doubtless due to a secondary reaction, namely, the reduction of a styrene derivative, $CH_2 \colon CHR$, which is also present in small amount among the products of the reaction. Two purely aromatic ketones, tetramethyldiamidobenzophenone (Michler's ketone) and its tetrethyl analogue, resemble the mixed ketones in that they yield carbinols. The ketones used were prepared by condensing an acid chloride with an aromatic hydrocarbon in the presence of freshly prepared aluminium chloride (Friedel-Craft's reaction); light petroleum was found to be a suitable medium in which to effect this. In almost all the reactions described in the paper, the product was eventually distilled under diminished pressure. The substances obtained are enumerated below.

Diphenylmethane, CH_2Ph_2. Parabenzyltoluene, $CH_2Ph\cdot C_6H_4Me$. *Parabenzoylcumene*, $CPhO\cdot C_6H_4\cdot CHMe_2$, boils at 334—336° under ordinary pressure, at 203—204° under 20 mm., and has a sp. gr. = 1·0364 at 18°/4°; *paraisopropyldiphenylmethane*, $CH_2Ph\cdot C_6H_4\cdot CHMe_2$, boils at 310° under ordinary pressure, at 176° under 13 mm., and has a sp. gr. = 1·007 at 18°/4°. Benzoylpseudocumene, $CPhO\cdot C_6H_2Me_3$, [Me:CPhO = 1:2:4:5], boils at 328° under normal and at 211° under 23 mm. pressure, and has a sp. gr = 1·0332 at 18°/4°; *benzylpseudocumene*, $CH_2Ph\cdot C_6H_2Me_3$, boils at 308—312° under ordinary pressure, at 190—191° under 20 mm., and has a sp. gr. = 1·0151 at 18°/4°. Benzoylmesitylene, $CPhO\cdot C_6H_2Me_3$, [Me_3:CPhO = 1:3:5:2]; benzylmesitylene, $CH_2Ph\cdot C_6H_2Me_3$. Parethoxybenzophenone, $CPhO\cdot C_6H_4\cdot OEt$, boils at 242° under 40 mm. pressure; *parethoxydiphenylmethane*,

$$CH_2Ph\cdot C_6H_4\cdot OEt,$$

boils at 317°, 217°, and 203° under ordinary pressure, 37 mm. and 12 mm. respectively, and could not be hydrolysed.

Tetramethyldiamidobenzhydrol, $OH\cdot CH(C_6H_4\cdot NMe_2)_2$. *Tetrethyldiamidobenzhydrol*, $OH\cdot CH(C_6H_4\cdot NMe_2)_2$, melts at 78°, and yields, with hydroxylamine and sodium hydrogen carbonate in alcoholic solution, a substance which melts at 128—129°, and contains 11·6 per cent. of nitrogen.

Phenylmethylcarbinol, $CHMePh\cdot OH$, boils at 203·6° (corr.) under 745·4 mm., at 118° under 40 mm., and has a sp. gr. = 1·007 at 21°; the *benzoate* boils at 189° under 20 mm. pressure, and under pressures greater than 25 mm. breaks up more or less into styrene and benzoic acid; the *phenylcarbamate* melts at 94°. The ethylbenzene also obtained in the reduction of acetophenone when added to bromine to which a little aluminium has been added previously, yields a *tetrabromo*-substitution derivative melting at 138—139°. Acetylpseudocumene, $C_6H_2Me_3Ac$ [Me_3:Ac = 1:2:4:5], boils at 137—138° under 20 mm. pressure, and has a sp. gr. = 1·001 at 18°/4°; its *oxime* melts at 85—86°; *trimethylphenethylol*, $OH\cdot CHMe\colon C_6H_2Me_3$, [$Me_3$:CHMe = 1:2:4:5], boils at 252—253° with slight decomposition under ordinary pressure, at 140—141° and 138° under 18 and 15 mm.; the *acetate* boils under the ordinary pressure at 254—257° with slight decomposition, and at 130° under 13 mm.; the *phenylcarbamate* melts at 108°; the *chloride* can be obtained, although only in an impure state, by treating the carbinol with phosphorus pentachloride at the ordinary temperature, or saturating it with gaseous hydrogen chloride at 0°; it boils at 125—129° under 13 mm. pressure, and loses hydrogen chloride when distilled under higher pressures. 1:2:4-*Trimethyl-5-vinylbenzene*, $CH_2\colon CH\cdot C_6H_2Me_3$, is obtained when the above mentioned acetate is boiled with methyl alcoholic potash; it distils over at 97° under 22 mm. pressure, and leaves a residue of a *polymeride* (α), which, after crystallisation from alcohol and light petroleum, melts at 118°. Moreover, the boiling point of the substance itself under atmospheric pressure, originally 212—214°, rises as the distillation is repeated, partial polymerisation no doubt taking place; and if hydrogen chloride be removed from the above-mentioned chloride by warming it gently with aniline, or if the corresponding carbinol be warmed with syrupy phosphoric acid, a second

polymeride (β), melting at 163°, is obtained. The unpolymerised substance forms a *dibromide*, which melts at 65—66°. Acetylmesitylene has a sp. gr. $= 0{\cdot}985$ at 18°/4°. *Trimethylphenethylol*, [Me_3:CHMe = 1:3:5:2], isomeric with the last carbinol, melts at 71°, and boils at 248° under ordinary pressure, at 141° under 24 mm.; the *acetate* boils at 252° under ordinary pressure, at 134—135° under 15 mm.; the *phenylcarbamate* melts at 124°; the (impure) *chloride* boils at 126—127° under 16 mm. pressure. 1:3:5-*Trimethyl*-2-*vinylbenzene* is obtained when the last-mentioned carbinol is treated with phosphoric anhydride, but not when the acetate is boiled with methyl alcoholic potash; it boils at 208—210° without polymerising, but is converted by 80 per cent. sulphuric acid into a *polymeride* which melts at 62°, and boils and decomposes slightly at 178—180° under 19 mm. pressure. This polymeride is also obtained when the chloride is warmed with aniline, it remains behind in the flask when the product is distilled with steam, whilst a small quantity of the unpolymerised substance passes over.

C. F. B.

Dimethylanilinephthaloylic Acid. By HEINRICH LIMPRICHT [and E. KÖNIG] (*Annalen*, 1898, **300**, 228—239).—*Dimethylanilinophthaloylic acid*, $NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, is obtained by adding aluminium chloride in small quantities at a time to a solution of phthalic anhydride and dimethylaniline in carbon bisulphide, and subsequently heating the mixture for 3—4 hours in a reflux apparatus; it melts at 205°, and separates from alcohol in two forms, one of which is anhydrous, the other containing 1 mol. of alcohol. The *barium* salt dissolves readily in water, and the *silver* salt melts at about 180° to a black liquid; the *hydrochloride* forms thin leaflets, and melts to a reddish-brown liquid at about 190°. The *nitroso*-derivative, $NMe_2{\cdot}C_6H_3(NO){\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, contains $1H_2O$, which is removed at 112—120°, the anhydrous substance melting at 164°; the *barium* salt forms red, prismatic crystals, which rapidly effloresce and become yellow on exposure to the air. Boiling caustic soda eliminates dimethylamine from the nitroso-derivative, giving rise to *nitrosophenolphthaloylic acid*, $OH{\cdot}C_6H_3(NO){\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, which separates from ethylic acetate in bright yellow, prismatic crystals, and melts at 178°.

Dimethylanilinophthalide, $CO{<}{}^{C_6H_4}_{-O-}{>}CH{\cdot}C_6H_4{\cdot}NMe_2$, is prepared by heating dimethylanilinophthaloylic acid with ammonia and zinc dust during 2 hours, and melts at 188°; it dissolves in caustic soda, but is almost insoluble in boiling sodium carbonate. The *nitroso*-derivative melts at 157°, and yields *nitrosophenolphthalide*,

$$CO{<}{}^{C_6H_4}_{-O-}{>}CH{\cdot}C_6H_3(NO){\cdot}OH,$$

under the influence of hot caustic soda; the latter nitroso-compound melts at 153°, and yields a *barium* salt when dissolved in baryta.

Dimethylanilinohydrophthaloylic acid, $NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}COOH$, produced on heating dimethylanilinophthaloylic acid with zinc dust and ammonia for 12 hours at 70—80°, melts at 173°; the *barium* salt forms small, white prisms. The *nitroso*-derivative crystallises from alcohol, and melts at 133°.

M. O. F.

Triphenylethanone (Benzoyldiphenylmethane). By A. GARDEUR (*Chem. Centr.*, 1897, ii, 660—662; from *Bull. Acad. roy. Belg.*, [iii], 34, 67—100).—From triphenylethanone, $CHPh_2\cdot COPh$, prepared by Delacre's method (*Compt. rend. Assoc. franç. Congrès de Pau*, 181) the author obtained the benzoyl derivative by heating it with benzoic chloride for 2—3 days at 240°, although attempts to prepare it by Saint Pierre's method (*Bull. Soc. Chim.*, [iii], 5, 292) failed. This compound does not combine with hydrogen bromide, yet its constitution probably corresponds with the enolic form, $CPh_2:CPh\cdot OBz$, for when reduced with sodium amalgam in alcohol, it yields triphenylethylic alcohol, $CHPh_2\cdot CHPh\cdot OH$. When the benzoyl derivative was treated with alkali, however, either no reaction took place, or triphenylethanone of the ordinary ketonic form was produced. Delacre's sodium compoundof triphenylethanone is a derivative of the ketonic type, for when heated with chlorobenzene, it yields triphenylmethane which can only result from the intermediate formation of tetraphenylethanone, $CPh_3\cdot COPh$. *Triphenylchlorethanone*, $CPh_2Cl\cdot COPh$, prepared by passing chlorine into an almost boiling solution of triphenylethanone in light petroleum, is a yellowish oil which, with water, forms triphenylethanolone, $OH\cdot CPh_2\cdot COPh$. This is best prepared, however, by heating triphenylbromethanone with silver benzoate for 24 hours at about 200°, and then hydrolysing the benzoate thus obtained. The benzoate crystallises from glacial acetic acid and alcohol in needles, and melts at 169°. By heating a solution of triphenylethanolone in glacial acetic acid with phenylhydrazine, small, crystalline needles of a substance which melts at 144°, and is probably the corresponding phenylhydrazone, are obtained. *Triphenylethanonephenylhydrazone*, which is prepared in a similar way, crystallises from glacial acetic acid in star-shaped needles, and melts at 156°. When triphenylbromethanone is reduced with zinc dust and glacial acetic acid, triphenylethanone and triphenylethylic alcohol, $CHPh_2\cdot CHPh\cdot OH$, are formed. The latter, when heated with benzoic chloride, forms a *benzoate* which crystallises from glacial acetic acid in needles, and melts at 145°. By the action of bromine in glacial acetic acid on triphenylethylic alcohol or its benzoate, *triphenylbromethylene*, $CPh_2:CBrPh$, is obtained; this crystallises from glacial acetic acid in needles, melts at 115° and with hydrogen bromide forms an unstable additive compound which melts at 106—110°, and with water yields triphenylethanone of the ordinary ketonic form. *Triphenylchlorethylene* obtained by the action of phosphorus pentachloride on triphenylethanone, crystallises from alcohol in short cylinders, and melts at 117°; when phosphorus pentabromide acts on triphenylethanone, triphenylbromethanone is formed. Triphenylethanediol (*triphenylethylenic glycol*), $OH\cdot CPh_2\cdot CHPh\cdot OH$, obtained in theoretical yield by the action of 10 times the calculated quantity of 7—8 per cent. sodium amalgam on a solution of triphenylethanolone in alcohol, crystallises in needles and melts at 164°; the *diacetyl* derivative crystallises from glacial acetic acid, and melts at 214°. Attempts to obtain triphenylethanone of the enolic form by withdrawing water from the glycol by means of hydrogen chloride, hydrogen bromide, or zinc chloride, yielded only the ordinary triphenylethanone. In one experiment, however, in which the glycol was melted with zinc

chloride, an oil was formed whose alcoholic solution, after remaining for a few days, deposited needles which melted at 100—102°, and appeared to be a mixture of the ordinary triphenylethanone with another substance, although the former alone was obtained on recrystallisation. When triphenylethylenic glycol is reduced with zinc and acetic acid, triphenylethanone is formed. By the action of potassium hydroxide and sodium acetate on the glycol, or by keeping it in a molten condition for some time, benzaldehyde and benzhydrol are obtained; in addition to these products, *benzhydrol ether*, $O(CHPh_2)_2$, which crystallises from alcohol in needles and melts at 118°, is formed when the glycol is submitted to dry distillation.

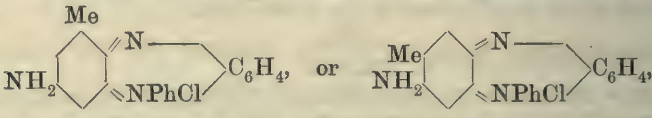
Triphenylethylenic oxide, $O<\begin{matrix}CPh_2\\|\\CHPh\end{matrix}$, prepared by the action of phosphoric anhydride on a solution of triphenylethylenic glycol in benzene, crystallises from glacial acetic acid in envelope-like crystals, melts at 105°, is stable in alkaline solutions, but in acid solutions or by recrystallisation is converted into the ordinary triphenylethanone.

E. W. W.

Aposafranines and Azonium Compounds from Tolusafranines. By Friedrich Kehrmann and Alexander Wetter (*Ber.*, 1898, **31**, 966—977).—The amido-group is best removed from Geigy's tolusafranine chloride by the following process. A solution of the chloride (60 grams) in the requisite quantity of boiling water is treated with dilute sulphuric acid so that a crystalline mass is obtained; this is cooled to 0°, and then treated with a little more than the theoretical quantity of sodium nitrite in concentrated aqueous solution; the resulting dark blue diazo-solution is gradually added to an equal volume of alcohol, also cooled to 0°, and the alcohol distilled; sulphuric acid (5 c.c.) is added to the dark red liquid, and the mixture allowed to remain for 12 hours. A crystalline mass, consisting of about equal quantities of methyl- and dimethyl-aposafranine derivatives, separates, and a considerable quantity of the dimethyl derivative remains in the mother liquor. The methylaposafranine is best purified by the aid of its chloride, which is much less soluble in dilute hydrochloric acid than the chloride of the dimethyl derivative. The separation is only completed after repeated solution in water and precipitation with dilute hydrochloric acid. *Methylaposafranine chloride*, $C_{19}H_{16}N_3Cl$, crystallises in long, pale yellow needles, is moderately soluble in water and readily in alcohol, yielding blood-red solutions; its alcoholic solution also exhibits a strong, light red fluorescence. Saturated aqueous solutions are completely precipitated on the addition of a few drops of dilute hydrochloric acid. Alkalis precipitate the base, but carbonates in dilute solution do not do so. Both in physical and chemical properties, the chloride resembles rosinduline chloride. The *nitrate* is also sparingly soluble in water, but practically insoluble in dilute nitric acid; the *platinochloride*, $(C_{19}H_{16}N_3)_2PtCl_6$, crystallises in small, reddish-brown plates, and is practically insoluble in water. The *acetyl* derivative of the chloride crystallises in long, yellowish-brown needles, which are soluble in water or alcohol, yielding yellowish-red solutions; the acetyl deriva-

tive differs completely from the corresponding derivative of aposafranine chloride (Abstr., 1896, i, 323). It yields very little amido-derivative, or tolusafranine chloride, when its alcoholic solution is allowed to remain in contact with ammonia for several days at the ordinary temperature, being merely hydrolysed. Aniline only reacts with the acetyl derivative when kept in contact with it for 14 days. The *platinochloride* of the acetyl derivative, $(C_{22}H_{20}N_3O)_2PtCl_6$, and the *nitrate*, $C_{22}H_{20}N_4O_4 + H_2O$, are described.

On account of the similarity between methylaposafranine and rosinduline, one of the following constitutions is suggested for the former,



in both of which the quinoid double bonds are on the heavier or basic side of the molecule. Monomethylaposafranine chloride is readily diazotised when suspended in 10 per cent. hydrochloric acid and treated with sodium nitrite; the diazotisation requires a longer time when a more dilute acid is employed. *Phenyltoluphenazonium* is obtained as its *iron double salt*, $C_{19}H_{15}N_2FeCl_4$, when the chloride is diazotised and the diazo-solution added to alcohol, and, at the end of 2 hours, precipitated with a saturated solution of ferric chloride in dilute hydrochloric acid, and may be best purified by washing with glacial acetic acid and subsequent crystallisation from the same solvent; it forms thick, brownish-red prisms melting at 150°, and dissolves readily in cold water and in hot acetic acid. The *nitrate*, $C_{19}H_{15}N_2{\cdot}NO_3$, obtained by precipitating the iron with ammonium carbonate, then adding dilute nitric acid, and salting out with solid sodium nitrate, also forms reddish-brown crystals. When the iron double salt is dissolved in alcohol (80 per cent.), and then treated with an excess of concentrated aqueous ammonia, a mixture of two isomeric methylaposafranines is obtained; the chief product is the methylaposafranine already described, but a small quantity of an isomeric substance is also formed, the chloride of which is more soluble in water, and crystallises in bronzy, glistening needles.

It is practically impossible to isolate pure dimethylaposafranine from Geigy's compound; even after repeated crystallisation, it always contains a quantity of the monomethyl derivative. When the impure dimethyl derivative is treated in the manner described above for the monomethyl derivative, a mixture of the double iron salts of methyl- and *dimethyl-phenylphenazonium chlorides* is formed. The dimethyl compound, $C_{20}H_{17}N_2FeCl_4$, is readily freed from the monomethyl compound, as it is much less soluble in glacial acetic acid; it crystallises in large, pale brown plates melting at 190°, and is readily soluble in water, but only sparingly in alcohol or acetic acid. The *nitrate*, $C_{20}H_{17}N_2{\cdot}NO_3$, and *platinochloride*, $(C_{20}H_{17}N_2)_2PtCl_6$, are also described. A concentrated solution of the iron double salt in alcohol (80 per cent.), when treated with an excess of concentrated ammonia and allowed to remain for 24 hours, yields *dimethylaposafranine*, the chloride of which crystallises in dark brown needles; its solutions in water or alcohol

have a magenta-red colour, and the latter exhibits a bright red fluorescence. The *platinochloride*, $(C_{20}H_{18}N_3Cl)_2PtCl_4$, and *acetyl* derivative are described. J. J. S.

Change of Position of the Double Linkings in Azonium Derivatives and its Causes. By FRIEDRICH KEHRMANN (*Ber.*, 1898, 31, 977—984).—Numerous facts seem to indicate that the quinoid double-bonds in azonium compounds can change their position; this supposition is rendered absolutely necessary if it be conceded that amines and alkalis always react with azonium compounds yielding derivatives with the substituting groups in the quinoid nucleus (that is, in the benzene ring to which the double bonds are attached). The latter conclusion receives support from the fact that quinones themselves react with amines, yielding derivatives in which the substituting groups are attached to the same benzene nucleus as that to which the quinone oxygen atoms are attached.

The author compares the change in position of the quinoid bonds in azonium compounds to the mutual oxidation and reduction of quinones and quinols, the reaction being regarded as an intramolecular oxidation and reduction. It is shown that the same generalisations hold for the two cases. Several examples are given in illustration of the change in position of double linkings. J. J. S.

2 : 4-Tetrachloro-1 : 3-diketotetrahydronaphthalene. By E. C. THEODOR ZINCKE and G. EGLY (*Annalen*, 1898, 300, 180—205).—2 : 4-*Tetrachloro*-1 : 3-*diketotetrahydronaphthalene*, $C_6H_4<\begin{matrix}CO—CCl_2\\CCl_2\cdot CO\end{matrix}$, is obtained as a hydrate by passing chlorine into a suspension of the anilide, $C_6H_4<\begin{matrix}C(NHPh)\cdot CCl\\CCl———C\cdot OH\end{matrix}$ (Zincke and Kegel, Abstr., 1889, 268), in glacial acetic and hydrochloric acids. The *hydrate*, which contains $3H_2O$, is also produced by the action of chlorine on 1 : 3-dihydroxynaphthalene, and crystallises in thin, colourless plates; it sinters at 80°, melts to a clear liquid at about 90°, and intumesces at 100°. The anhydrous ketochloride, which is formed on exposing the hydrate to a vacuum, or to a temperature of 100—110°, crystallises in stellate groups of prisms, and melts at 92°.

The *methoxy*-compound, $C_6H_4<\begin{matrix}C(OH)(OMe)\cdot CCl_2\\CCl_2————C(OH)_2\end{matrix},H_2O$, is obtained by boiling a solution of the hydrate in methylic alcohol; it begins to sinter at 86°, melts to a clear, red liquid at 156°, and decomposes at 160°.

2 : 4-*Dichloro*-1 : 3-*dihydroxynaphthalene* (*dichloronaphtharesorcinol*), $C_6H_4<\begin{matrix}C(OH)\cdot CCl\\CCl—C\cdot OH\end{matrix}$, prepared by heating a solution of the hydrate in glacial acetic acid with concentrated hydrochloric acid and stannous chloride, crystallises from glacial acetic acid in colourless needles or nacreous leaflets, and melts at 138—139°. The *diacetyl* derivative melts at 136°. Phenylhydrazine gives rise to the *compound*, $C_6H_4<\begin{matrix}C(OH)——CCl\\C(N:NPh)\cdot C\cdot OH\end{matrix}$, which melts at about 190°; the *diacetyl* derivative melts at 150°.

Orthodichloracetylphenyldichloracetic acid, $CHCl_2{\cdot}CO{\cdot}C_6H_4{\cdot}CCl_2{\cdot}COOH$, obtained by the action of sodium carbonate on the ketohydrate, crystallises from benzene in colourless needles and small prisms, and melts at 106—107°. The *methylic* salt forms colourless needles, and melts at 114—115°. On heating the acid or the ketohydrate with sodium carbonate, β-dichloro-α-ketohydroxyhydrindenecarboxylic acid, $CO{<}^{CCl_2}_{C_6H_4}{>}C(OH){\cdot}COOH$ (Zincke and Gerland, Abstr., 1888, 1199), is produced.

Orthotrichloracetylphenyldichloracetic acid, $CCl_3{\cdot}CO{\cdot}C_6H_4{\cdot}CCl_2{\cdot}COOH$, is prepared by treating the ketohydrate with a solution of bleaching powder; it crystallises from benzene in colourless needles, or in monoclinic plates and melts at 135°, beginning to decompose at 150—160°. The *sodium* salt forms needles, and the *methylic* salt melts at 108—109°; the *anhydride* sublimes at 160° and melts at 224°, yielding dichloromethylenephthalyl. The action of hot sodium carbonate converts the acid into *trichloracetophenonecarboxylic acid*, $CCl_3{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, which melts at 139°; alkalis eliminate chloroform. The *hydroxylactone* of orthotrichloracetylphenyldichloracetic acid, $C_6H_4{<}^{C(OH)(CCl_3){\cdot}O}_{CCl_2\text{———}CO}$, is produced on boiling the acid with water, and forms large, monoclinic crystals; it melts and decomposes at 139°. The *acetyl* derivative crystallises from benzene in colourless prisms, melting at 170°. The hydroxylactone yields dichloromethylenephthalyl (Zincke and Cooksey, Abstr., 1890, 784) when heated with sodium acetate.

Orthocarboxyphenyldichloracetic (*dichlorohomophthalic*) *acid*,

$$COOH{\cdot}C_6H_4{\cdot}CCl_2{\cdot}COOH,$$

obtained on the action of potash on orthotrichloracetylphenyldichloracetic acid dissolved in methylic alcohol, crystallises from hot, dilute nitric acid in white needles, and from benzene in colourless plates melting at 141°, with formation of the *anhydride*, which melts at 130°. Aqueous alkalis convert the acid into orthocarboxybenzoylformic acid. M. O. F.

Reduction Products of Azo-compounds. VIII. By PAUL JACOBSON and ANDREW TURNBULL (*Ber.*, 1898, **31**, 890—906. Compare Abstr., 1896, i, 23).—It has previously been shown that whereas benzeneazophenetoil readily yields an orthosemidine on reduction with a hydrochloric acid solution of stannous chloride, benzeneazo-metacresetoil undergoes the same transformation much less readily, the difference having been ascribed to the presence of the methyl group in the ortho-position relatively to the azo-group. On the other hand, Witt and Helmholt have found (Abstr., 1894, i, 606) that benzeneazo-α-naphthylic ethylic ether very readily yields an orthosemidine derivative when it is reduced with stannous chloride, and the product then treated with hydrochloric acid. The authors have applied this method of reduction to all three compounds, and have found that, under these circumstances also, the orthosemidine forms 81 per cent. of the total semidine derivatives obtained from benzeneazophenetoil, 50 per cent. of the total obtained from benzenazometacresetoil, and 100 per cent. of that from benzeneazonaphythlic ethylic ether; thus showing that the reaction is not influenced by the substitution of the naphthalene ring for the

simpler benzene ring. Benzeneazo-*ar*-tetrahydronaphthylic ethylic ether, however, behaves in a similar manner to the metacresetoil derivative, the orthosemidine amounting to only 50 per cent. of the total semidines obtained. The reduced ring of the naphthalene molecule, therefore, exerts an influence similar to that of a methyl group. *Benzeneazo*-ar-*tetrahydronaphthylic ethylic ether*, $PhN_2\cdot C_{10}H_{10}\cdot OEt$, prepared by the action of sodium ethoxide and ethylic iodide on the corresponding naphthol, crystallises in orange-red prisms which have a golden lustre and melt at 91·5°. That this compound actually has the constitution assigned to it, is shown by the fact that benzeneazo-*ar*-tetrahydronaphthol, from which it is prepared, is converted by reduction, followed by oxidation, into tetrahydro-α-naphthaquinone. On reduction, it yields the ortho- and para-semidine derivatives, as well as a smaller amount of *paramido*-ar-*tetrahydronaphthylic ethylic ether*, which crystallises from light petroleum in long, colourless needles melting at 60°. The *orthosemidine* derivative, 4-*amido*-3-*anilido*-1-*ethoxy*-1′ : 2′ : 3′ : 4′-*tetrahydronaphthalene*, $C_6H_8<\begin{matrix}C(OEt):CH\\C(NH_2):C\cdot NHPh\end{matrix}$, crystallises from light petroleum in colourless plates or needles, which become pink on exposure to the air and melt at 168—169°. The corresponding *azimide*, $OEt\cdot C_{10}H_9<\begin{matrix}NPh\\N\end{matrix}>N$, crystallises in colourless, oblique tablets, melts at 125—126°, and can be sublimed without decomposing. The *stilbazonium base*,

$$OEt\cdot C_{10}H_9<\begin{matrix}NPh(OH)\\N{=\!=}CPh\end{matrix}>CPh,$$

forms yellow prisms and melts at 151·5°. The *methenyl* compound, $OEt\cdot C_{10}H_9<\begin{matrix}NPh\\N\end{matrix}>CH$, which is obtained by heating the base with formic acid, crystallises in thin plates melting at 139°, and yields a sparingly soluble nitrate. The carbon bisulphide derivative, $OEt\cdot C_{10}H_9<\begin{matrix}NPh\\N\end{matrix}>C\cdot SH$, is only slowly formed and melts at 269—270°, whilst the *orthohydroxybenzylidene* derivative,

$$OEt\cdot C_{10}H_9:N_2HPh\cdot CH\cdot C_6H_4\cdot OH,$$

prepared from salicylaldehyde, crystallises in yellow prisms melting at 130—131°. The orthosemidine is converted by oxidation with ferric chloride into *anilidotetrahydro-α-naphthaquinone*, $C_6H_8<\begin{matrix}CO\cdot CH\\CO\cdot C\cdot NHPh\end{matrix}$ which forms brownish-red crystals melting at 164°.

The parasemidine derivative, *paramidophenylparethoxytetrahydro*-ar-*α-naphthylamine*, $C_6H_8<\begin{matrix}C(OEt){=\!=\!=}CH\\C(NH\cdot C_6H_4\cdot NH_2)\end{matrix}>CH$, crystallises in colourless prisms, melts at 87—88°, and becomes bluish on exposure to the air. The *sulphate* is only very sparingly soluble in water, whilst the *hydrochloride* dissolves more readily. This base gives the characteristic reactions of a parasemidine with nitrous acid, ferric chloride, chromic acid, and lead peroxide. The *monacetyl* derivative, $C_{20}H_{24}N_2O_2$, crystallises in colourless needles melting at 177—178°, and the thiocarbamide, $(OEt\cdot C_{10}H_{10}\cdot NH\cdot C_6H_4\cdot NH)_2CS$, crystallises in plates melting at 201°.

Tetrahydronaphtholdis-azobenzene, $OH\cdot C_{10}H_9(N_2Ph)_2$, is formed in the preparation of benzeneazo-*ar*-tetrahydro-*a*-naphthol, and melts at 156°.

A. H.

Orientation in the Terpene Series: Conversion of Monocyclic Terpenes into the corresponding Derivatives of Benzene. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1898, 31, 1401—1405). —The authors have devised a general method by which monocyclic terpenes may be converted into the corresponding derivatives of benzene; it depends on the ultimate bromination of the terpene dihydrobromide, followed by reduction of the product with zinc and hydrochloric acid. It is found more convenient to brominate the dihydrobromides with bromine in presence of iodine, it being then unnecessary to raise the temperature as in using the halogen in presence of iron.

On this principle, paracymene and metacymene have been obtained from limonene and carvestrene respectively.

The passage from carone to carvestrene is now explained. Caronic acid has been recently synthesised by Perkin and Thorpe (Proc., 1898, 107), in a manner which proves that it has the constitution assigned to it by von Baeyer (Abstr., 1897, i, 83). The production of dihydrocarvone, $CHMe{<}{\begin{smallmatrix}CO-CH_2\\CH_2\cdot CH_2\end{smallmatrix}}{>}CH\cdot CMe{:}CH_2$, from carone $\begin{smallmatrix}CHMe\cdot CO\cdot CH\\ |\qquad\quad\ \ |\\ CH_2-CH_2\cdot CH\end{smallmatrix}{>}CMe_2$, on the one hand, and the conversion of carylamine, $\begin{smallmatrix}CHMe\cdot CH(NH_2)\cdot CH\\ |\qquad\qquad\qquad |\\ CH_2 \text{———} CH_2\cdot CH\end{smallmatrix}{>}CMe_2$, into carvestrene,

$$CH_2{<}{\begin{smallmatrix}CMe:CH\\CH_2\cdot CH_2\end{smallmatrix}}{>}CH\cdot CMe{:}CH_2,$$

on the other, represent the two directions which the rupture of the trimethylene ring is capable of following.

M. O. F.

Action of Sulphuric Acid on *l*-Terebenthene. By GUSTAVE BOUCHARDAT and J. LAFONT (*Compt. rend.*, 1897, 125, 111—114).—By the action of sulphuric acid on lævo-terebenthene, and subsequent treatment with alcoholic potash, a number of products are obtained, among which are two potassium salts both readily soluble in water. The less soluble of the two, *potassium terebenthene sulphate*, $C_{10}H_{16}SHKO_4$, crystallises in colourless plates somewhat resembling boric acid. Its rotatory power in alcoholic solution is $[a]_D = -25$. Its aqueous solution is stable in the presence of a little alkali, but in neutral or acid solution readily undergoes decomposition, yielding potassium hydrogen sulphate and *l*-borneol. Nitric acid oxidises it to *l*-camphor melting at 203°. The second potassium salt has the same composition, but crystallises in silky needles, and its rotatory power is $[a]_D = +10°$. It is decomposed in neutral or acid aqueous solution, yielding sulphuric acid and the alcohol melting at 45°, previously called isoborneol, but which the authors state to be *d*-fenchol. Nitric acid oxidises this potassium salt or the alcohol obtained from it to liquid camphor, identical with that obtained by the oxidation of synthetical isoborneol.

J. J. S.

Ethereal Oil of Pine Wood. By PETER KLASON (*Bied. Centr.*, 1898, **27**, 137—138; from *Svensk. kem. tidskr.*, 1897, **9**, 138—140).—The oil obtained by the steam distillation of pine resin was found to be almost pure pinene. On the other hand, the oil extracted from pine wood by means of acid sulphite solution proved to be cymene. No terpenes are present in pine wood oil. N. H. J. M.

A Crystalline Dicamphene Hydride. By ALEXANDRE ÉTARD and GEORGES MEKER (*Compt. rend.*, 1898, **126**, 526—529).—Terebenthene hydrochloride (100 parts) is heated until it just melts, sodium (15 parts) is introduced in one lot and the mixture well shaken so as to granulate the molten sodium; the reaction should take place slowly and at as low a temperature as possible. When the reaction is complete, the mixture is extracted with benzene and then fractionated, when two portions, one distilling at 150—160°, and a second at 320—330°, are obtained. The heavier fraction is mixed with a little benzene and agitated with fuming sulphuric acid. After well washing first with Nordhausen, then with concentrated sulphuric acid, and finally with water, the substance is distilled, when, if the liquid is well cooled, 15—20 per cent. of a crystalline substance is obtained. These crystals consist of *dicamphene hydride*, $C_{20}H_{34}$, and belong to the regular system, sp. gr. = 1·001 at 15°; it melts at 75°, boils at 326—327° (uncorr.), and has specific rotatory power $[\alpha]_D = +15° 27'$. [Letts obtained in this way a crystalline dicamphene hydride, $C_{20}H_{34}$, melting at 94°, and boiling at 321—323·6° (Abstr., 1880, 669); to this no reference is made.—A. J. G.] J. J. S.

The Rhodinol Question. By JULIUS BERTRAM and EDUARD GILDEMEISTER (*Ber.*, 1898, **31**, 749).—Poleck has no right to complain (this vol., i, 263) that the name of *geraniol* has been substituted for his name of *rhodinol*. What Eckart called rhodinol was a mixture of 70 per cent. of geraniol with 20 of *l*-citronellol and 10 of non-alcoholic substances of unknown composition. C. F. B.

Action of Ethylic Oxalate on Camphor. III. By J. BISHOP TINGLE (*Amer. Chem. J.*, 1898, **20**, 318—342. Compare Trans., 1890, 652; Abstr., 1897, i, 484).—When camphoroxalic acid is boiled with acetic anhydride, there are produced, in small amounts, (*a*) a *substance* crystallising in clusters of colourless, slender needles melting at 242—242·5°, the nature of which has not been ascertained; (*b*) a *substance*, probably an anhydride, crystallising from light petroleum in slender needles melting at 190°; and (*c*) *acetylcamphoroxalic acid*,

$$C_8H_{14}<\begin{matrix}C:C(OAc)\cdot COOH, \\ | \\ CO\end{matrix}$$

crystallising from benzene in reticulated, stellate, needle-shaped prisms melting at 133·5—134·5°. It reacts speedily with bromine vapour, liquefying, and then gradually giving off hydrogen bromide, but no crystalline compound could be obtained.

Bromine vapour acts on camphoroxalic acid, producing a *bromo*-acid, $C_{12}H_{15}O_4Br$, as an oil which gradually solidifies to crystalline nodules melting at 130°. The *silver* and *copper* salts are described. Magnesium amalgam removes the bromine from the acid, giving a substance melting

at 84—84·5°, which resemble camphoroxalic acid in general properties. The crystals are, however, not identical and will be further examined.

Camphoroxalic acid reacts with benzoic chloride, forming a substance melting at 192—193°, apparently identical with the supposed anhydride produced by the action of acetic anhydride as stated above; with benzoic anhydride, camphoroxalic acid reacts at 150° with evolution of carbonic anhydride, but no definite product could be isolated.

When quickly distilled under ordinary pressure, camphoroxalic acid evolves carbonic anhydride, and some camphor is formed, but the major portion passes over unchanged. Heating with barium hydroxide in a current of dry hydrogen causes hydrolysis to take place at the double linking, with production of barium oxalate and camphor.

Phenylhydrazine camphoroxalate, prepared by the interaction of the components, separates from alcohol in minute, colourless needles darkening when heated to 205°, and melting and evolving gas at 214—215°; its alcoholic solution gives a red coloration with ferric chloride and a purple with concentrated nitric acid.

When camphoroxalic acid is heated in sealed tubes with dilute sulphuric or hydrochloric acid at 135—150° for several hours, an *acid*, $C_{12}H_{20}O_6$, is formed which crystallises from benzene in clusters of colourless needles melting at 92—93°. It differs from camphoroxalic acid in not yielding any sparingly soluble salts, in not dissolving readily in light petroleum, and in giving a deep blue coloration with alcohol and ferric chloride.

Pure *ethylic camphoroxalate*, prepared by heating the acid with very dilute alcoholic hydrogen chloride, crystallises from light petroleum in fern-like aggregates of long needles melting at 40·5°. It does not form a copper salt, and is miscible with ether in all proportions. With dry ammonia, it gives a sparingly soluble, white *substance*, darkening when heated to 200°, and melting at 225°; with hydroxylamine, a *substance* crystallising from a mixture of toluene and light petroleum in colourless slender needles, melting at 120—121°; with acetic anhydride, acetylcamphoroxalic acid; with bromine, an *additive* compound, which evolves hydrogen bromide, forming a substance resembling the bromocamphoroxalic acid already described. With benzoic chloride or benzoic anhydride, however, no benzoyl derivative could be obtained, thus indicating a greater stability of the ethylic salt than of the free acid.

Methylic camphoroxalate, $C_8H_{14}<\begin{matrix}C:C(OH)\cdot COOMe \\ | \\ CO\end{matrix}$, prepared by the action of methylic oxalate on camphor, according to instructions given in a previous paper (*loc. cit.*), separates from light petroleum in long, arborescent needles melting at 74·5—75°; it resembles the ethylic salt in general properties. The *phenylhydrazide* forms slender, white needles melting at 204—205°, which, when acted on by glacial acetic acid, give *methylic camphylphenylpyrazolecarboxylate*,

$$C_8H_{14}<\begin{matrix}C\text{———}C\cdot COOMe, \\ \| \qquad\quad \| \\ C\cdot NPh\cdot N\end{matrix}$$

crystallising in colourless needles, and melting at 80·5—81·5°. The

sodium salt is without marked physiological action, whereas the sodium salt of camphoroxalic acid is rapidly toxic.

iso-Amylic camphoroxalate separates in needle-shaped crystals melting at 98·5—99·5°. It gives a sparingly soluble *phenylhydrazide.*

A comparison of the crystallographic characters of camphoroxalic acid and its methylic and isoamylic salts shows that the grade of symmetry of the crystals becomes lower as the molecular weight increases.

The compound obtained by the interaction of phenylhydrazine and camphoroxalic acid is shown to be a phenylhydrazide, as it is readily oxidised with mercuric oxide to give a *substance* crystallising in colourless, monoclinic plates melting at 112°.

When camphylphenylpyrazolecarboxylic acid is distilled with barium hydroxide, a yellowish-green oil passes over, which gives Knorr's pyrazoline reaction, and probably contains camphylphenylpyrazole

$$C_8H_{14}<\begin{matrix}C\text{—}CH\\ \|\\ C\cdot NPh\end{matrix}>N.$$

A. W. C.

Substances contained in Sesame Oil, and their Relation to the Characteristic Colour Reactions of the Oil. By VITTORIO VILLAVECCHIA and GUIDO FABRIS (*Chem. Centr.*, 1897, ii, 772—773; from *Ann. Lab. chim. centr. delle Gabelle*, 3, 13—26).—Baudouin's colour reaction for sesame oil with hydrochloric acid and cane-sugar is also readily obtained with all those sugars which easily yield furfuraldehyde, and the authors assume this substance to be the cause of the reaction. As a test for sesame oil, they use a 1 per cent. solution of furfuraldehyde in 95 per cent. alcohol with hydrochloric acid, which forms an intense red coloration with the oil. From sesame oil, they have isolated the following substances. (1) *Sesamin*, $(C_{11}H_{12}O_3)_2$, crystallises from alcohol in long, colourless needles, from chloroform in prisms, is insoluble in water, light petroleum, ether, alkalis, and mineral acids, easily soluble in chloroform, benzene, and glacial acetic acid, melts at 123°, has a specific rotatory power $[\alpha]_D = 68·36$ at 22°, does not give the furfuraldehyde reaction, does not combine with iodine, forms neither acetyl nor phenylhydrazine derivatives, and is not attacked by potassium hydroxide, hydrochloric acid, or oxidising agents, but, with nitric acid of sp. gr. = 1·4, yields two crystalline compounds which melt at 235° and 145° respectively. (2) A higher alcohol, $C_{25}H_{44}O + H_2O$, which crystallises from alcohol in colourless leaflets having a nacreous lustre, melts at 137·5°, has a specific rotatory power $[\alpha]_D = -34·23$ at 20°, does not give the furfuraldehyde reaction, combines readily with bromine and iodine, yields an acetyl derivative which is a crystalline powder insoluble in water, very easily soluble in benzene, melts at 130—131°, and is easily saponified. (3) A viscous, odourless oil, which is very easily soluble in alcohol, ether, chloroform, and glacial acetic acid, insoluble in water and mineral acids, and very slightly soluble in alkalis. This substance gives the colour reaction with furfuraldehyde and hydrochloric acid.

E. W. W.

Aloins. By EUGÈNE LEGER (*Compt. rend.*, 1897, 125, 185—188).—Analyses of barbaloin made by the author agree best with Groenewold's formula (Abstr., 1890, 639); it always crystallises with $1H_2O$. When treated in pyridine solution with benzoic chloride, it yields an

amorphous dibenzoyl derivative, $C_{16}H_{14}Bz_2O_7$, which is readily soluble in alcohol or ether. A diacetyl derivative may be obtained in a similar manner. Barbaloin, partially purified by crystallisation from methylic alcohol, contains another aloin, apparently isomeric with barbaloin, and crystallising from methylic alcohol in yellow, opaque plates containing $3H_2O$. J. J. S.

Aromatic Principles of Capsicum annuum, L., and Capsicum fastigiatum, Bl. By JOHANNES MÖRBITZ ((*Chem. Centr.*, 1897, ii, 593; from *Pharm. Zeit. Russ.*, 36, 299—301, 313—316, 327—331, 341—346, 369—376).—The cayenne fruit contains 0·05—0·07 per cent. of *capsacutin*, $C_{35}H_{54}N_3O_4$, which is obtained by freeing the powdered fruit from fat by means of light petroleum, extracting with ether, hydrolysing the residue left on evaporating the extract, again extracting with ether, evaporating, and finally crystallising the residue from boiling light petroleum. Capsacutin has an extremely pungent taste, which may be detected in a solution containing only 1 part in 11,000,000; it is only slightly soluble in water and light petroleum, but soluble in the ordinary solvents. It is neither a glucoside nor an acid. E. W. W.

2-Methylpyrrolidine. By GOTTFRIED FENNER and JULIUS TAFEL (*Ber.*, 1898, 31, 906—914).—The 2-methylpyrrolidine prepared from methylpyrrolidone by reduction with amylic alcohol and sodium (Neugebauer and Tafel, Abstr., 1889, 1015) probably contained a little piperidine derived from impurities in the amylic alcohol and the authors have therefore prepared the pure compound by the same method, but using amylic alcohol which had been carefully purified, and have compared the properties of this substance with those of the 2-methylpyrrolidine derived from the 1:2-dimethylpyrrolidine, which is formed by the action of hydrochloric acid on dimethylpiperidine (Merling, Abstr., 1891, 1506; Ladenburg, Mugdan and Brzostovicz, Abstr., 1894, i, 555), the two compounds being found to be in all respects identical. 2-Methylpyrrolidine has a sp. gr. = 0·84 at 20°/20°, and boils at 95·5—96·5° under a pressure of 744 mm. The hydrochloride is very deliquescent, and melts at the temperature of the water bath, whilst the *oxalate* melts at 178—179°; the *platinochloride*, $(C_5H_{12}N)_2PtCl_6$, has no definite melting point, and the *aurochloride*, $C_5H_{12}NAuCl_4$, melts at 158—161°. Dimethylpyrrolidine boils at 96—96·5°, and yields 2-methylpyrrolidine when its hydrochloride is heated in hydrogen chloride. Both methyl- and dimethyl-pyrrolidine are converted by methylic iodide into the methiodide of dimethylpyrrolidine, whilst the corresponding methochloride is formed by molecular change from dimethylpiperidine hydrochloride. *Trimethylpyrrolidineammonium platinochloride* forms yellow, octahedral crystals, and decomposes at 240—250°, whilst the *aurochloride* begins to decompose at 204°. The aurochloride $(C_5H_{12}NCl)_2AuCl_3$, which was formerly ascribed to methylpyrrolidine, is in reality derived from piperidine.

A. H.

Condensing Action of Ammonia and Organic Amines in Reactions between Aldehydes and Ethylic Acetoacetate. By EMIL KNOEVENAGEL (*Ber.*, 1898, 31, 738—748).—The author's conclusions are reproduced below.

I. Nitrogenous products (dihydropyridine derivatives,

$$CHR<\begin{matrix}C(COOEt):CMe\\C(COOEt):CMe\end{matrix}>NH),$$

are obtained: (1) from an aldehyde, ethylic acetoacetate, and free ammonia; (2) from an aldehyde-ammonia and ethylic acetoacetate (Hantzsch's dihydropyridine synthesis), or from a hydramide [trialkylidenediamine, $(R\cdot CH)_3N_2$] and ethylic acetoacetate together with ammonia; (3) from an aldehyde and ethylic β-amidocrotonate; (4) from ammonia and a mixture of an ethylic alkylideneacetoacetate, CHR:CAc·COOEt, with ethylic acetoacetate; (5) from an ethylic alkylideneacetoacetate and β-amido- or a β-monalkylamido-crotonate.

II. Non-nitrogenous products (at low temperatures, ethylic alkylideneacetoacetates, CHR:CAc·COOEt; at higher temperatures, ethylic alkylidenediacetoacetates, $CHR(\cdot CHAc\cdot COOEt)_2$, are obtained: (1) from a mixture of an aldehyde and ethylic acetoacetate under the influence of a mon- or di-alkylamine (or of ammonia at a low temperature); (2) from an alkylidenebisdialkylamine, $R\cdot CH(NR_2)_2$, and ethylic acetoacetate; (3) from an aldehyde and an ethylic β-dialkylamidocrotonate; (4) from an ethylic alkylideneacetoacetate and ethylic acetoacetate, under the influence of alkyl- and dialkyl-amines; (5) from an ethylic alkalideneacetate and an ethylic β-dialkylamidocrotonate.

It appears that in Hantzsch's dihydropyridine synthesis, the aldehyde-ammonia first reacts with the ethylic acetoacetate to form ethylic ethylideneacetoacetate, ammonia being liberated, and the ammonia converts the second molecule of the acetoacetate into ethylic β-amidocrotonate, which reacts with the ethylideneacetate to form ethylic dihydrocollidinedicarboxylate. All these separate stages can be realised, at any rate to a certain extent. If this view be correct, one of the weightiest arguments in favour of Riedel's pyridine formula, $CH<\begin{matrix}CH:CH\\CH:CH\end{matrix}>N$, is seriously impaired.

Ethylic β-piperidocrotonate, $C_5NH_{10}\cdot CMe:CH\cdot COOEt$, is described for the first time. It is made by mixing piperidine (1 mol.) with ethylic acetoacetate (1 mol.), removing the oil after 3 hours, drying it over dehydrated sodium sulphate, and distilling it under diminished pressure. It boils at 169° under 15 mm. pressure. C. F. B.

Syntheses in the Pyridine Series. I. An Extension of Hantzsch's Dihydropyridine Synthesis. By EMIL KNOEVENAGEL and A. FRIES (*Ber.*, 1898, 31, 761—767).—When ethylic benzylidenemalonate, $CHPh:C(COOEt)_2$ (1 mol.), is heated with ethylic β-amidocrotonate, $NH_2\cdot CMe:CH\cdot COOEt$ (1 mol.), for 9 hours at 130—150° in a reflux apparatus under 40 mm. pressure, the product is *ethylic 6-oxy-4-phenyl-2-methyltetrahydropyridine-3:5-dicarboxylate*,

$$NH<\begin{matrix}CMe:C(COOEt)\\CO\cdot CH(COOEt)\end{matrix}>CHPh,$$

or the corresponding enolic form, and the yield of the crude substance is 75 per cent. of the theoretical. The new compound, which melts at 149·5—150°, is hardly soluble in acids or alkalis, and when boiled with strong hydrochloric acid for 10 hours, yields γ-acetyl-β-phenyl-

butyric acid, $COMe\cdot CH_2\cdot CHPh\cdot CH_2\cdot COOH$ (Vorländer, Abstr., 1894, i, 528).

When the heating is continued for 18 hours at 130—150°, and then for 9 hours at 150—170°, there is obtained, besides the substance described above, a compound which apparently has the constitution $CMe\Big<\begin{matrix}C(COOEt)\cdot CHPh\\ NH\text{————————}CO\end{matrix}\Big>CH\cdot CO\cdot NH\cdot CMe{:}CH\cdot COOEt$, and must have been formed by the action of 2 mols. of the amidocrotonate on 1 mol. of the benzilidenemalonate; this compound melts at 179—180°, and also yields acetylphenylbutyric acid when it is boiled with hydrochloric acid. Two other products, melting at 206—206·5° and 262—263° respectively, were obtained in addition; these have been shown (following abstract) to be identical with the products of the action of ethylic malonate itself on ethylic β-amidocrotonate.

Ethylic ethylidenemalonate reacts in a similar manner to the benzylidene analogue, yielding with ethylic β-amidocrotonate a compound, $NH\Big<\begin{matrix}CMe{:}C(COOEt)\\ CO\cdot CH(COOEt)\end{matrix}\Big>CHMe$, which is closely related to the substance obtained by Collie (Trans., 1897, 301, 303; compound A) by heating the hydrochloride of ethylic β-amidocrotonate. C. F. B.

Syntheses in the Pyridine Series. II. Action of Ethylic Malonate on Ethylic β-Amidocrotonate. By Emil Knoevenagel and A. Fries (*Ber.*, 1898, 31, 767—776. Compare preceding abstract).—When pure ethylic malonate (1 mol.) is heated with ethylic β-amidocrotonate (1 mol.) and alcoholic sodium ethoxide (1 mol.) for 7—9 hours in a sealed tube at 140—150°, a product is obtained which is presumably ethylic dioxymethyltetrahydropyridinecarboxylate,

$$NH\Big<\begin{matrix}CMe{:}C(COOEt)\\ CO\text{————}CH_2\end{matrix}\Big>CO \quad \text{or} \quad NH\Big<\begin{matrix}CMe\text{=====}CH\\ CO\cdot CH(COOEt)\end{matrix}\Big>CO,$$

or the enolic form of either of these. It melts at 206—206·5°, and has both acid and basic properties; its rather unstable *hydrochloride*, with $3H_2O$, melts at 152° when heated quickly; further, it yields a *monobromo*-substitution derivative which melts and decomposes at 245°, and also a compound containing very much more bromine (70·5 per cent.); it forms a *dioxime*, which carbonises at 245—255°; and when boiled with aqueous or alcoholic potash, or strong hydrochloric acid, or when its hydrochloride is heated alone, 4 : 6-dihydroxy-2-methylpyridine (Collie, Trans., 1891, 617; 1892, 723) is obtained. This substance has feeble basic, but pronounced acid properties; the *potassium* salt crystallises with 1EtOH.

If the heating be carried out in a reflux apparatus at 130—150° under a pressure of 40 mm., 2 mols. of the amidocrotonate appear to react with 1 mol. of the malonate, the product being *ethylic 2 : 4 : 4′-trihydroxy-2′-methylquinoline-3-carboxylate*,

$$\begin{array}{l}COOEt\cdot C{:}C(OH)\cdot C\cdot C(OH){:}CH\\ \quad\;\; OH\cdot C{:}CH\text{——}C\cdot N\text{===}CMe\end{array}.$$

This melts at 262—263°, dissolves in strong hydrochloric acid, but not in alkalis, and loses carbonic anhydride when boiled with alcoholic or aqueous potash, the product, which remains unmelted at 360°, being presumably *2 : 4 : 4′-trihydroxy-2′-methylquinoline*. C. F. B.

Syntheses in the Pyridine Series. III. Some Acetylpyridines and Acetyldihydropyridines. By EMIL KNOEVENAGEL and WALTER RUSCHHAUPT (*Ber.*, 1898, 31, 1025—1033).—3 : 5-*Diacetyl*-4-*phenyl*-2 : 6-*dimethyl*-$\Delta_{2,5}$-*dihydropyridine*, $C_5NH_2Me_2PhAc_2$, is obtained by heating benzylideneacetylacetone (Abstr., 1895, i, 50) (1 mol.) with amidoacetylacetone (1 mol.) for 2 hours on a boiling water bath; it is yellow, melts at 180°, and boils at 225—235° under 25 mm. pressure. Dilute nitric acid at 60—70° oxidises the two hydrogen atoms, forming 3 : 5-*diacetyl*-4-*phenyl*-2 : 6-*dimethylpyridine*, which melts at 188°

Ethylic 3-*acetyl*-4-*phenyl*-2 : 6-*dimethyl*-$\Delta_{2,5}$-*dihydropyridine*-5-*carboxylate* is obtained by heating either ethylic benzylideneacetoacetate (Abstr., 1896, i, 232) with amidoacetylacetone, or ethylic β-amidocrotonate with benzylideneacetylacetone; it is yellow, melts at 167°, and boils at 210—230° under 25—30 mm. pressure. Dilute nitric acid, at temperatures slightly below 40°, oxidises it to *ethylic* 3-*acetyl*-4-*phenyl*-2 : 6-*dimethylpyridine*-5-*carboxylate*, which melts at 85—86°.

Ethylideneacetylacetone, $CHMe\colon C(CMeO)_2$, was obtained by passing gaseous hydrogen chloride for ½ hour into a dilute chloroform solution of acetaldehyde (1 mol.) and acetylacetone (1 mol.), and then distilling off the chloroform under diminished pressure at 0°; it boils at 87°, 92°, and 97° under 10, 13, and 18 mm. pressure respectively. When it is mixed with amidoacetylacetone, 3 : 5-*diacetyl*-2 : 4 : 6-*trimethyl*-$\Delta_{2,5}$-*dihydropyridine* is obtained; this is yellow, melts at 152°, and boils with some decomposition at 220—230° under 20 mm. pressure.

Methylamidoacetylacetone, $NHMe\cdot CMe\colon CH\cdot CMeO$, prepared by mixing 33 per cent. aqueous methylamine with acetylacetone, melts at 45°, and boils at 200°. When mixed with ethylideneacetylacetone, it forms 3 : 5-*diacetyl*-1 : 2 : 4 : 6-*tetramethyl*-$\Delta_{2,5}$-*dihydropyridine*, which is greenish-yellow and melts at 118°.

When diacetyltrimethyldihydropyridine, or ethylic acetyltrimethyldihydropyridinecarboxylate, is boiled for 4 hours with 10 per cent. caustic potash, it is converted into 1 : 3-dimethyl-Δ_6-ketotetrahydrobenzene (Hantzsch, Abstr., 1883, 84; Knoevenagel, Abstr., 1895, i, 52) :—$NH<^{CMe\colon CAc}_{CMe\colon CAc}>CHMe + 3H_2O = NH_3 + 3CH_3\cdot COOH +$ $CH<^{CMe\cdot CH_2}_{CO—CH_2}>CHMe$. Diacetylphenyldimethyldihydropyridine and ethylic acetylphenyldimethyldihydropyridinecarboxylate are scarcely attacked. With 40 per cent. caustic soda, ethylic acetyltrimethyldihydropyridinecarboxylate yields, in addition to the product mentioned above, a substance which melts at 86° and boils at 155—160° under 15 mm. pressure, and appears to be somewhat impure ethylic trimethyldihydropyridinecarboxylate.

Methylenediacetylacetone (Scholtz, this vol., i, 43) was obtained in crystals incidentally; it melts at 87°. C. F. B.

Action of Concentrated Alkalis on Ethylic Dihydrocollidinedicarboxylate [2 : 4 : 6-Trimethyl-Δ_2-dihydropyridinedicarboxylate]. By OTTO COHNHEIM (*Ber.*, 1898, 31, 1033—1037).—When this substance is heated with 60—75 per cent. aqueous potash, the

volatile products distill, over at once, more water being added as required; the main product is ethylic trimethyldihydropyridinecarboxylate, which is a solid, melting at 89—90°, and boiling at 140—160° under 15 mm. pressure when still impure, and possessing scarcely any basic properties, unlike the isomeride which Hantzsch obtained, employing hydrochloric acid instead of potash, which was a basic oil. Some 3 : 5-dimethyl-Δ_2-ketotetrahydrobenzene (compare preceding abstract) is formed in addition. When an upright tube 60 cm. long is inserted between the flask and the condenser, so that only the more volatile products escape at once from the action of the potash, a small quantity of an oil is obtained which seems to be a mixture of trimethyldihydropyridine with a little trimethylpyridine.

C. F. B.

Action of Formaldehyde on Tetrahydroquinoline. By Carl Goldschmidt (*Chem. Zeit.*, 1897, **21**, 243).—A compound, $CH(C_9NH_{10}Cl)_3$, is formed when a solution of tetrahydroquinoline in concentrated hydrochloric acid is warmed for 10 minutes on the water bath with the requisite quantity of formaldehyde and ferric chloride. It is salted out, filtered, and washed with water, and further purified by solution in alcohol and precipitation with ether. It dyes silk green, and unmordanted cotton a greenish-blue, but not of a sufficiently strong tint to be of use. It is readily soluble in hot water, and with alkalis yields a brown base.

J. J. S.

Action of Tannin and of Gallic Acid on Quinoline Bases. By William Oechsner de Coninck (*Compt. rend.*, 1897, **125**, 37—38. Compare Abstr., 1897, i, 447, 570).—Pure dry tannin readily dissolves in freshly distilled lepidine, and a red colour is only produced after prolonged exposure to the air and light. Gallic acid reacts in a similar manner, and no difference is observed when solutions of lepidine in absolute alcohol or in dry ether are employed. An aqueous solution of tannin immediately yields a white, curdy precipitate with pure lepidine. Quinoline and quinaldine react in exactly the same manner as lepidine, and in this respect resemble pyridine bases and various volatile alkaloids.

J. J. S.

Amido-2′-hydroxylepidine and Lepidinic Acid. By Emil Besthorn and H. Byvanck (*Ber.*, 1898, **31**, 796—804).—When metaphenylenediamine (1 mol.) is heated with ethylic acetoacetate (rather more than 1 mol.) in a sealed tube for 5—6 hours up to 130°, *amido-2′-hydroxylepidine* (*amido-2′-hydroxy-4′-methylquinoline*), [$NH_2 = 2$, or perhaps 4] is formed; it melts at 270°. From metatolylenediamine, *amido-2′-hydroxymethyllepidine* is obtained in a similar manner; it melts above 300°. When the amidohydroxylepidine is boiled with phosphorus oxychloride, a pale yellow *amido-2′-chlorolepidine* is obtained; this melts at 142—143°, and can be converted into 2′-chlorolepidine by first transforming it into the hydrazine hydrochloride, and then boiling the free hydrazine base with copper sulphate in aqueous solution. By diazotising the amidohydroxylepidine and then heating the solution (see also below), pale yellow *hydroxy-2′-chlorolepidine* is obtained; this melts at 214—215°, and is oxidised by alkaline permanganate to

2′-*chlorolepidinic acid*, which melts and decomposes at 181—182°, crystallises with $2H_2O$, and is reduced by boiling with hydriodic acid, potassium iodide, and amorphous phosphorus to lepidinic (4-methylpyridine-5 : 6-dicarboxylic) acid.

When amido-2′-chlorolepidine is diazotised and the solution heated, *dihydroxylepidine* is formed, in addition to chlorhydroxylepidine; this is also formed when amido-2′-hydroxylepidine is diazotised, and the aqueous solution heated; it decomposes at 270°. Oxidation with alkaline permanganate converts it into 2′-*hydroxylepidinic acid*, melting and decomposing at 252—253°, but the yield is poor. C. F. B.

Morpholine Derivatives. By RICHARD STOERMER and MAX FRANKE (*Ber.*, 1898, **31**, 752—760; compare Abstr., 1897, i, 473).—1′ : 2′-*Dimethylphenomorpholine*, $C_6H_4<\begin{matrix}O\text{——}CH_2\\ NMe\cdot CHMe\end{matrix}$, was obtained in the following manner. 2′-Methylphenomorpholine is allowed to remain for several days with methylic iodide, and the product is made alkaline and extracted with ether. The extract is then freed from ether by distillation, and the residue is benzoylated and shaken with ether and hydrochloric acid, when benzoylmethylphenomorpholine remains dissolved in the ether and the dimethylphenomorpholine in the acid. The latter boils at 259—261°, has an odour like that of naphthalene, and gives a carmine coloration with ferric chloride; the *hydrochloride* melts at 170°, the brownish-yellow unstable *platinochloride* at 144—146° with decomposition (in the presence of excess of platinum tetrachloride, another reddish-white salt, melting at 116° is formed), and the greenish-yellow *picrate* at 136°. By acidifying with hydrochloric acid the alkaline liquid that is left after the extraction with ether described above, evaporating to dryness, extracting the dry residue with absolute alcohol, and precipitating with ether, *trimethylphenomorpholonium iodide*, $C_6H_4<\begin{matrix}O\text{———}CH_2\\ NMe_2I\cdot CHMe\end{matrix}$, melting at 170°, is obtained.

The tertiary base, $C_9H_{13}NO_3$ or $C_9H_{12}NO_3$, formed along with methylphenomorpholine when orthonitrophenoxyacetone, in boiling alcoholic solution, is reduced with tin and hydrochloric acid (*loc. cit.*), is now found to contain chlorine, and is shown to be 3-*chloro*-2′-*methylphenomorpholine*; for it can be synthesised by boiling the potassium salt of nitrochlorophenol [$OH : Cl : NO_2 = 1 : 3 : 6$] with chloracetone and acetone, and reducing the *chloronitrophenoxyacetone* formed (which melts at 86°, its *semicarbazone* at 195°) in boiling alcoholic solution with tin and hydrochloric acid. Its *hydrochloride* melts at 105—106°, and is readily decomposed by water; the lemon-yellow *nitrosamine* melts at 96·5°, and the *phenylcarbamide*, $NHPh\cdot CO\cdot C_8NOH_6MeCl$, at 148°.

2-*Nitro*-1-*naphthoxyacetone*, $NO_2\cdot C_{10}H_6\cdot O\cdot CH_2\cdot COMe$, is obtained by heating the potassium salt of 2-nitro-1-naphthol with chloracetone and acetone for 12 hours at 100° in a sealed tube; it is yellowish and melts at 145°; the yellow, unstable *phenylhydrazone* melts at 120°, the yellowish-white *semicarbazone* at 208°, and the *oxime* at 158°. When reduced in boiling alcoholic solution with tin and hydrochloric acid, it yields *methylnaphthamorpholine*, $C_{10}H_6<\begin{matrix}O\text{—}CH_2\\ NH\cdot CHMe\end{matrix}$, melting at 95·5°;

the *hydrochloride* melts at 229°, and is readily decomposed by water; the unstable, brownish-yellow *platinochloride* melts at 237°, the lemon-yellow *nitrosamine* (only to be obtained by adding the calculated quantity of amylic nitrite to an alcoholic solution of the base containing a little hydrochloric acid) at 190—195° with decomposition, the *phenylcarbamide* at 180°, and the *acetyl* and *benzoyl* derivatives at 124° and 183·5° respectively. C. F. B.

Mercury Haloid Compounds of Antipyrine. By M. C. SCHUYTEN (*Chem. Centr.*, 1897, ii, 614—615; from *Bull. Acad. roy. Belg.*, [iii], **33**, 821—842).—The mercuric chloride compound, $C_{11}H_{12}N_2O,HgCl_2$, is most soluble in alcohol and water, least soluble in ether, and dissolves in hot benzene, toluene, and carbon bisulphide; the solutions are neutral. When the aqueous solution is evaporated, small, crystalline needles separate, from the other solutions only amorphous residues are obtained. The mercuric bromide compound, $C_{11}H_{12}N_2O,HgBr_2$, is obtained as a white, amorphous precipitate on mixing alcoholic solutions of the two substances; when heated, it melts at 103°, then turns slowly garnet-red, finally charring and giving off fumes of mercuric bromide. It dissolves in alcohol, benzene, and toluene, and is slightly soluble in water, chloroform, ether, and carbon bisulphide.

The mercuric cyanide compound, $C_{11}H_{12}N_2O,HgCy_2$, obtained by mixing hot concentrated aqueous solutions of the components, crystallises in transparent prisms which, on heating, become opalescent at 160—165° and melt at 224°; the yellow, molten mass, on further heating, chars and emits white fumes. The mercury is only incompletely precipitated by sodium peroxide, whilst from the other mercury compounds complete precipitation is effected. According to the author, in these compounds one atom of halogen is directly united to nitrogen, since (1) only one molecule of antipyrine is contained in the compound, whereas other similar mercury haloid compounds usually contain two; (2) with mercurous chloride, antipyrine forms the hydrochloride, mercury, and mercuric oxide; and (3) mercuric iodide, which is not as easily dissociated as the other haloids, does not combine with antipyrine. E. W. W.

Generalisations as to Melting Points among Pentacyclic Nitrogen Compounds. By EDGAR WEDEKIND (*Ber.*, 1898, **31**, 949—953).—The author points out that, just as in the case of substituted malonic acids, so with the phenyl derivatives of tetrazole, the symmetrical compounds melt at relatively higher temperatures than the less symmetrical derivatives.

Malonic acid	134°	Tetrazole	156°
Methylmalonic acid	130	N-(1)-Phenyltetrazole	an oil
Dimethylmalonic acid	180	C-(3)-Phenyltetrazole	212—213
Methylisopropylmalonic acid	106—107	Diphenyltetrazole	106—107

Another generalisation is that phenyl derivatives of 5-ring nitrogen compounds, in which the phenyl group is attached to nitrogen, melt at a much lower temperature than the isomeric compounds in which the phenyl group is attached to carbon.

Pyrazole	70°	Glyoxalin	90°
N-(1)-Phenylpyrazole	11	N-Phenylglyoxalin	13
C-(3)-Phenylpyrazole	78	N-Phenylpyrroline	62
C-(4)-Phenylpyrazole	228	C-Phenylpyrroline	129

The same generalisation applies to alkyl, &c., derivatives.

Pyrroline	131°	Glyoxaline	89°
N-(1)-Methylpyrroline	113	N-Methylglyoxaline	−5
C-(2)-Methylpyrroline (α)	148	C-Methylglyoxaline	137
C-(3)-Methylpyrroline (β)	143		
Triazole	121	Tetrazole	156
C-Methyltriazole	94	N-Methyltetrazole	145

The introduction of nitrogen in place of carbon in a cyclic compound tends to raise the melting point.

Pyrroline (1N), liquid; pyrazole (2N), m. p. 70°; glyoxaline (2N), m. p. 89°; triazole (3N), m. p. 121°; tetrazole (4N), m. p. 156°. An exception to this is osotriazole, which melts at 22°, and yet has a very symmetrical formula.

The molecular weights of tetrazole, C-amidotetrazole, and of diphenyltetrazole have been determined, and the numbers indicate that each compound is monomolecular. J. J. S.

Decomposition of 2 : 5-Diphenyltetrazole into Bladin's N-Phenyltetrazole. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 942—948).—*Orthohydroxybenzylideneamidoguanidine acetate*,

$$OH\cdot C_6H_4\cdot CH{:}N\cdot NH\cdot C(NH)\cdot NH_2,CH_3\cdot COOH,$$

is obtained as follows. Amidoguanidine nitrate (11·2 grams) is dissolved in the least possible quantity of cold water, and the solution then well shaken with salicylaldehyde (10 grams), and finally with concentrated potassium hydroxide, until it has an alkaline reaction; when the odour of the aldehyde has disappeared, the solution is acidified with concentrated acetic acid, and on rubbing the sides of the vessel, the acetate is deposited in the form of a crystalline powder. It is best purified by suspending it in hot benzene and then bringing it into solution by the addition of hot alcohol; at the end of 24 hours, large, colourless crystals are obtained, which, after several recrystallisations, melt at 191—192°. The salt is readily soluble in warm water or alcohol, and sparingly in benzene, acetone, chloroform, or light petroleum; its aqueous solution gives a green coloration with ferric chloride, and with phenyldiazonium chloride it yields a red, gelatinous precipitate melting at 176—177°. This compound, when treated with concentrated nitric acid at 85°, yields an extremely explosive nitro-derivative. 5-*Paramidodiphenyltetrazole*, $NH_2\cdot C_6H_4\cdot C{<}\begin{matrix}N\cdot NPh \\ | \\ N{:}N\end{matrix}$, is obtained when the finely powdered nitro-derivative (this vol., i, 336) is reduced with stannous chloride and hydrochloric acid; it is extracted from the alkaline liquid by the aid of chloroform, and purified by repeated recrystallisation from dilute alcohol; it crystallises from ether or dilute acetone in colourless prisms melting at 156°. Its *hydrochloride* crystallises in long, colourless needles, and is practically insoluble in water; the *nitrate*, *acetate*, and *sulphate*, melting at 224—225°, are also described. When diazotised and the diazo-solu-

tion boiled with water, 5-*parahydroxydiphenyltetrazole* is obtained, and, after several recrystallisations from hot water, melts at 190—191°; it crystallises from ether in colourless, glistening needles, is readily soluble in alkalis or warm ammonium hydroxide, dissolves in benzene, alcohol, warm ether, acetone, chloroform, or acetic acid, and is sparingly soluble in warm water, nitric acid, or light petroleum. Bladin's phenyltetrazolecarboxylic acid, $COOH{\cdot}C{<}\begin{matrix}N{\cdot}NPh\\ |\\ N{:}N\end{matrix}$, is obtained when amidodiphenyltetrazole nitrate is oxidised with potassium permanganate. 2-Phenyltetrazole is obtained when the carboxylic acid is heated in an oil bath at 150—170°. J. J. S.

Action of Diphenyltetrazochloride on Acetoacetic Acid, and on Benzaldehydephenylhydrazone. By EDGAR WEDEKIND [and PAUL BLUMENTHAL] (*Annalen*, 1898, **300**, 239—258. Compare Abstr., 1897, i, 443).—*Cycloformazyl methyl ketone*, $COMe{\cdot}C{<}\begin{matrix}N{\cdot}NH{\cdot}C_6H_4\\ |\\ N{=}N{\cdot}C_6H_4\end{matrix}$, prepared by the action of diphenyltetrazochloride on acetoacetic acid, is a brownish-red, amorphous powder without definite melting point. The *phenylhydrazone*, which crystallises from a mixture of chloroform and petroleum, melts at about 205—210°; it is insoluble in alkali, and the solution in concentrated sulphuric acid is brownish-red. Phenylhydrazine also yields another *compound*, which melts at 197°, and dissolves in alkali; it forms a carmine-red solution in concentrated sulphuric acid.

Paraphenylformazylbenzene (*formazyldiphenyl*),

$$NHPh{\cdot}N{:}CPh{\cdot}N{:}N{\cdot}C_6H_4Ph,$$

obtained by the action of diphenyltetrazochloride on benzaldehydephenylhydrazone under the influence of alcoholic potash, is a greenish-violet, crystalline powder with bronze reflex, and melts at 174°. The solution in concentrated sulphuric acid is red, and becomes yellowish-brown when heated.

Paraphenylhydroxyazobenzene, $OH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4Ph$, is produced on adding an alcoholic solution of diphenyltetrazochloride to a solution of phenol in caustic potash; the solution in concentrated sulphuric acid is carmine-red. It begins to sinter at about 240°.

Diformazylbenzene, $C_{12}H_8(N{:}N{\cdot}CPh{:}N{\cdot}NHPh)_2$, prepared by the action of diphenyltetrazochloride on the phenylhydrazone of benzoylformic acid, crystallises from dilute alcohol in needles, and melts at 153°. Oxidation converts it into *bistriphenyltetrazolium hydroxide*, which sinters at 260—278°, remaining solid at 285°; alkaline reducing agents regenerate diformazylbenzene. M. O. F.

Derivatives of Cinchonine. By EDOUARD GRIMAUX (*Compt. rend.*, 1898, **126**, 575—578).—The bromomeroquinenine hydrobromide, $C_9H_{14}BrNO_2 + HBr$, obtained by Kœnigs by the action of bromine on the crude product of the oxidation of cinchonine and quinine, loses only one atom of bromine when treated with silver nitrate at the ordinary temperature. When treated with picric acid or potassium picrate, it yields the salt $C_9H_{14}BrNO_2,C_6H_3(NO_2)_3{\cdot}OH$, which crystallises in yellow lamellæ melting at 203—204°, and is only slightly soluble in

cold water. The nitroso-derivative, $C_9H_{13}BrNO_2 \cdot NO$, obtained by the action of nitrous acid on the hydrobromide, forms nacreous crystals which melt at 87·5—88°. When the hydrobromide is heated with concentrated aqueous potash, it yields nacreous plates of the compound $C_9H_{14}BrNO_2 + KBr$.

By heating the hydrobromide with water and zinc powder, impure meroquinenine is obtained, and this yields an acetyl derivative, $C_9H_{14}NO_2Ac$, which forms small, white crystals melting at 112·5°.

Hydroxymeroquinenine is obtained by the action of excess of silver hydroxide on the hydrobromide; it crystallises from a mixture of methylic alcohol and ether in small, white crystals insoluble in ether and chloroform, but very soluble in water and methylic and ethylic alcohols. It decomposes without melting, and its solutions have an alkaline reaction. C. H. B.

Yohimbehe Bark and Yohimbine. By HERMANN THOMS (*Chem. Centr.*, 1897, ii, 978—979; from *Ber. pharm. Ges.*, 7, 279—283).—From a sample of bark named Yumbehoa, the author obtained 0·54 per cent. of a mixture of two alkaloids, from which Spiegel's yohimbine (*Chem. Zeit.*, 1896) was separated by means of benzene. The other alkaloid forms a green fluorescent solution in chloroform, but could not be obtained in a crystalline state. According to Prof. Schumann, this bark is almost certainly identical with yohimbehe bark. The leaves of the Yumbehoa tree also contain yohimbine. E. W. W.

An Oxyptomaine. By WILLIAM OESCHNER DE CONINCK (*Compt. rend.*, 1898, 126, 651—653).—The ptomaine, $C_8H_{11}N$ (Abstr. 1888, 730 and 1118), when treated with very dilute hydrogen peroxide in the dark, yields an oxyptomaine, $C_8H_{11}NO$, together with yellowish, resinous products. The oxyptomaine is a non-deliquescent, white solid, which softens at 250°, melts at a slightly higher temperature, and decomposes suddenly at about 260°. It dissolves readily in acids, and forms a crystallisable hydrochloride, $C_8H_{11}NO,HCl$, and a corresponding platinochloride, both of which are gradually decomposed when boiled with water.

When heated with zinc powder, the oxyptomaine yields the original base, $C_8H_{11}N$ which is a collidine, and hence the oxy-derivative may be called *collidone*. It is the higher homologue of the oxypyridines previously described. C. H. B.

A New Enzyme—Caroubinase. By JEAN EFFRONT (*Compt. rend.*, 1897, 125, 116—118).—The carbohydrate caroubin (this vol., i, 398) is readily hydrolysed by dilute acid, and also by a special diastase, *caroubinase*, which is produced during the fermentation of the seeds; the secretion of the enzyme is somewhat slow during the actual period of fermentation, and increases with the formation of chlorophyll. Alcohol precipitates the active principle from infusions of the growing germs. Caroubinase acts energetically at 40°, its maximum activity being at about 45—50°, but becoming very feeble at 70°, and the enzyme is completely destroyed at 80°. An addition of 0·01—0·03 per cent. of formic acid increases the hydrolytic power of the enzyme. The sugar obtained by the hydrolysis of caroubin with this enzyme is not identical with that formed under the influence of dilute acids. J. J. S.

Peptone Salts from Glutin. By CARL PAAL (*Ber.*, 1898, **31**, 956—966. Compare Abstr., 1892, 895).—The author has made further experiments with three peptone hydrochlorides of different composition obtained from glutin. The peptone salt (20 grams), dissolved in 5 times its weight of water, was dialysed during 3 days into a litre of water, which was renewed daily; the contents of the dialyser and of the outer vessel were then separately evaporated in platinum vessels, and the residues dried by heating their methylic or ethylic alcoholic solutions in a vacuum. About 12 grams of one salt was found to have diffused; this portion was readily soluble in ethylic alcohol, whereas the salt which had not diffused was practically insoluble in ethylic alcohol but dissolved readily in cold methylic alcohol. The two salts also differed materially in their composition and also in molecular weight.

The author has succeeded in isolating the substances which are not precipitated when the peptone salts are treated with phosphotungstic acid; these were obtained in the form of a thick syrup, and were partially precipitated by alcohol, and completely by ether, in yellowish lumps. The dried substance gave 6·26 per cent. of ash, which consisted entirely of lime obtained from the barium hydroxide used. The substance gave a strong biuret reaction.

Glutin peptone barium (Ba = 9·25 per cent.) and ferropeptone were obtained from the peptone contained in the phosphotungstic acid precipitate. When the peptone salt is boiled with absolute ethylic alcohol and saturated with hydrogen chloride, a salt is obtained containing a rather higher percentage of hydrogen chloride, probably brought about by the water produced during etherification, as it has already been shown that peptone hydrochlorides are fairly readily etherified. J. J. S.

Crystallisation of Animal Proteids. By F. GOWLAND HOPKINS and STANISLAW N. PINKUS (*J. Physiol.*, 1898, **23**, 130—136).—If an equal bulk of saturated solution of ammonium sulphate is added to white of egg, the fixed alkali of the proteid liberates ammonia, and this interferes with the separation of crystals; if, however, this is neutralised with acetic acid, the process of crystallisation is much accelerated; and still more is this the case if a slight excess of the acid is added. Evaporation is then unnecessary to obtain crystals, and there can be no confusion between them and crystals of ammonium sulphate; their affinity for carbol-magenta or methylene blue is also distinctive, should any confusion arise. Analogous results were obtained with serum albumin. W. D. H.

Action of Superheated Water on Proteid. By RICHARD NEUMEISTER (*Zeit. Biol.*, 1898, **36**, 420—424).—The points of difference between Salkowski (this vol., ii, 173) and the author are explained as being chiefly due to the former's imperfect acquaintance with the published work of the latter. W. D. H.

Organic Chemistry.

Mixed Fluorine and Bromine Derivatives Containing Two Atoms of Carbon. By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1897, ii, 1098—1099; from *Bull. Acad. roy. Belg.*, [iii], **34**, 307—326. Compare *ibid.*, **33**, 439—474).—When a mixture of 200 grams of difluorotetrabromethane with 34 grams of antimony trifluoride and 20 grams of bromine is heated for 30 hours at 130° in a platinum apparatus, *difluorotribromethane*, $CBr_2F{\cdot}CHBrF$, and a small quantity of *trifluorodibromethane*, $CBrF_2{\cdot}CHBrF$, are formed; the latter is a rather volatile, colourless liquid with an odour like that of carbon tetrachloride, is not affected by light, and boils at 81·5°. The former is a colourless liquid which turns yellow under the influence of light, has a pleasant odour, is insoluble in water, does not attack glass, becomes turbid when exposed to moist air, does not burn, boils at 146°, has a sp. gr. = 2·60772 at 17·5°, 2·60277 at 20°, and a specific refractive index = 1·50787 at 17·5°. When a cooled alcoholic solution is reduced with zinc-dust and the evolved vapours collected in alcohol at −10° or −25°, *difluorobromethylene*, $CBrF{\colon}CHF$, is obtained as a colourless, limpid, and extremely volatile liquid which is not affected by light, boils at 19·6° under 770 mm. pressure, has a sp. gr. = 1·84337 at 0° and a specific refractive index = 1·3846 at 0°. It combines very energetically with bromine, forming difluorotribromethane, and oxidises slowly to an acid which contains fluorine, and is very deliquescent. When sodium ethoxide acts on difluorotribromethane, *difluorodibromethylene*, $CBrF{\colon}CBrF$, is formed with considerable rise of temperature; this is a colourless liquid, has an unpleasant odour, is not affected by light, boils at 70·5° under 771 mm. pressure, has a sp. gr. = 2·31212 at 20°, and a specific refractive index = 1·45345 at 20°. It combines readily with oxygen with considerable liberation of heat, forming *fluorodibromacetic fluoride*, $CBr_2F{\cdot}COF$, from which *fluorodibromacetic acid*, $CBr_2F{\cdot}COOH$, may be obtained by the action of water. The *sodium* salt of this acid is deliquescent, very soluble in water, and soluble in alcohol; the *barium* salt is crystalline, deliquescent, and soluble in alcohol, and the *amide* crystallises in white needles, is slightly soluble in water and easily so in ether. *Ethylic fluorodibromacetate*, prepared by the action of water and alcohol on fluorodibromacetic fluoride, is a liquid with the odour of peppermint. Difluorodibromethylene does not undergo polymerisation; when it is dissolved in chloroform and treated with bromine, *difluorotetrabromethane*, $CBr_2F{\cdot}CBr_2F$, is formed; this is a white, volatile, crystalline substance, has a strong odour of camphor, is easily soluble in alcohol, soluble in acetic acid, melts at 62·5°, and boils at 186·5° under 758 mm. pressure.

By the replacement of bromine by fluorine in an unsaturated compound, the boiling point is lowered constantly by about 10°; in

saturated compounds, the boiling point is also lowered. In some cases, the replacement of hydrogen by fluorine increases the stability of the molecule, thus tetrabromethane cannot be distilled under the ordinary pressure, whilst fluorotetrabromethane, under these conditions, is only slightly decomposed, and difluorotetrabromethane requires to be heated to a temperature very much above the boiling point before it decomposes. E. W. W.

Specific Gravity of Iodoform. By F. Beyerinck (*Chem. Zeit.*, 1897, **21**, 853).—Recrystallised iodoform has sp. gr. = 4·008 at 17°. Saturated solutions of iodoform in bromoform have a specific gravity = 2·97, and are useful in mineral separations. J. J. S.

Alkylic Isocyanurates; Formula and Constitution of Cyanuric Acid. By Paul Lemoult (*Compt. rend.*, 1897, **125**, 869—871).—Methylic isocyanurate, $C_3N_3O_3Me_3$, prepared by Wurtz's method, crystallises in voluminous crystals melting at 175°. The author confirms Wurtz's statement that the ethylic salt melts at 95°; Limbricht and Habich found it to melt at 85°.

The following thermochemical data have been obtained.

	Molecular heat of combustion. (1) At constant volume.	(2) At constant pressure.	Heat of formation.
Methylic salt ...	704·22 Cal.	703·8 Cal.	172·5 Cal.
Ethylic ,, ...	1167·83 ,,	1168·27 ,,	197·9 ,,

The differences between the heats of combustion of the two salts at constant pressure (3 × 154·8) indicates that they are true homologues. The difference, however, between the methylic salt and free cyanuric acid (compare Abstr., 1896, ii, 11) shows that the methyl groups in the salt cannot be attached to carbon, but agrees better with the supposition that they are attached to nitrogen. The constitution of the acid is then $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>NH$, a formula which agrees with the decomposition of the acid into carbonic anhydride and ammonia under the influence of alkalis. J. J. S.

Action of Alkylic Haloids on Mercaptides. By Karl A. Hofmann and W. O. Rabe (*Zeit. anorg. Chem.*, 1898, **17**, 26—34. See also Abstr., 1897, i, 310).—*Mercury mercaptoiodide*, HgI·SEt, obtained by cautiously warming mercury mercaptide with ethylic iodide, crystallises in slender, pale yellow needles, and is not decomposed when boiled for an hour with water or alcohol. When treated with concentrated sulphuric acid, either cold or hot, no iodine or hydrogen iodide is liberated; with boiling sodium hydroxide, it is converted into an orange-coloured compound which contains mercaptan and mercury, but no halogen; and with concentrated potassium cyanide, it yields mercury cyanide and mercaptan. It is also obtained by the action of mercaptan on an alcoholic solution of mercury iodide, and by mixing alcoholic solutions of mercury mercaptide and mercury iodide.

When the mixture of mercury mercaptide and ethylic iodide is

heated for some time at 80—100°, an oily mixture of the double compounds, HgI_2,SEt_3I and $HgI_2,2SEt_3I$, is obtained. They are separated by crystallisation from acetone, in which, at ordinary temperatures, the former compound only is soluble; this melts at 107·5° and has been described in a previous paper. The *compound*, $HgI_2,2SEt_3I$, obtained alone when mercury mercaptide with excess of ethylic iodide is heated under pressure for 80 hours at 75°, separates from alcohol or acetone in white crystals, and melts at 147°.

The action of ethylic bromide on mercury mercaptide takes place in a manner analogous to that of ethylic iodide. *Mercury mercapto-bromide*, HgBr,SEt is obtained at the ordinary temperature, or better by warming the mixture at 40—50°; it crystallises from alcohol in colourless tablets, turns yellow at 190°, and sinters at 202—203°. The *compound*, $HgBr_2,SEt_3Br$, obtained together with the following compound by heating the mixture under pressure for 48 hours at 75°, and separated by prolonged fractional crystallisation from acetone and methylic alcohol, crystallises in thin, lustrous plates belonging to the monosymmetric system, and melts at 104°. The *compound* $HgBr_2,2SEt_3Br$ was not obtained free from the preceding compound; it melts at 139—145°.

Mercury mercaptonitrate, $NO_3\cdot Hg\cdot SEt$, obtained by leading nitric oxide, prepared from sodium nitrite and fuming nitric acid, through an alcoholic solution of mercury mercaptide, is a white powder insoluble in water, alcohol, and all ordinary solvents; it carbonises when heated, with the formation of a mercury mirror. When it is dissolved in hydrochloric acid, mercaptan is evolved; it yields a clear solution in cold, concentrated sulphuric acid, which, on heating, yields mercuric sulphate and nitrogen peroxide, and reacts with sodium hydroxide and potassium cyanide in a manner analogous to the mercury mercaptohaloids. It is also obtained by mixing solutions of mercury nitrite and mercury mercaptide and as an intermediate product in the oxidation of mercury mercaptide with concentrated nitric acid.

The *compound* $(HgBr\cdot SEt)_2,NH_3$, obtained by treating mercury mercaptobromide suspended in absolute alcohol or ether with dry ammonia, is a white, amorphous powder, turns yellow when gently heated, and carbonises at a higher temperature with the formation of a mercury mirror; it yields ammonia when treated with sodium hydroxide, and mercaptan when treated with hydrochloric acid.

The *compound* $HgNO_3SEt,NH_3$, is obtained from mercury mercaptonitrate in a similar manner to the preceding compound, which it closely resembles in properties, except that it crystallises in lustrous plates.

Mercury mercaptoiodide does not combine with ammonia, even when heated at 100° with concentrated ammonia under pressure; this is not surprising when one remembers the instability of the ammonia compounds with mercuric iodide. E. C. R.

Action of Phosphoric Acid on Glycerol. By ADRIAN and AUGUSTE TRILLAT (*J. Pharm.*, 1898, [vi], 7, 226—230).—Glycerophosphoric acid, obtained by decomposing its barium salt with sulphuric

acid, invariably contains a large proportion of barium hydrogen glycerophosphate; attempts to obtain the pure acid by decomposing the potassium salt with tartaric acid, and the lead and copper salts by hydrogen sulphide, failed on account of the simultaneous formation, in the former case of potassium hydrogen glycerophosphate, and in the latter of phosphoric acid. When glycerophosphoric acid is liberated from its barium salt by a slight excess of sulphuric acid, and the solution concentrated, either by boiling or by slow evaporation, gradual decomposition takes place, glycerol and phosphoric acid being formed.

When the proportions given by Portes and Prunier (*J. Pharm.*, 1894, 393) for preparing calcium glycerophosphate are employed, a limit of the action, corresponding with a limit of etherification, occurs when 21 per cent. of glycerophosphoric acid has been produced. In addition to the latter, there appears to be formed a *diglycerophosphoric acid*, $H(C_3H_7O_2)_2PO_4$, which is neutral to methyl-orange, but becomes strongly acid when boiled with alcohol or water, owing to the formation of glycerophosphoric and phosphoric acids. W. A. D.

Caroubinose. By JEAN EFFRONT (*Compt. rend.*, 1897, **125**, 309—311).—Caroubinose, the sugar obtained by the hydrolysis of caroubin with mineral acids (this vol., i, 398), is a non-crystallisable syrup, soluble in alcohol or water, and having the composition $C_6H_{12}O_6$. It differs from *d*-glucose in its rotatory power, which is $[\alpha]_D = 24$. When caroubin is not completely hydrolysed to caroubinose, an intermediate, white, amorphous substance is obtained; this is insoluble in 95 per cent. alcohol, but dissolves in water, and is non-fermentable. When caroubinose is treated in the usual manner with phenylhydrazine hydrochloride and sodium acetate, a mixture of a phenylhydrazone and an osazone is obtained. The *phenylhydrazone*, $C_{12}H_{18}N_2O_5$, forms pale yellow prisms which sink to the bottom of the liquid; it is best purified by washing with boiling absolute alcohol, which removes any osazone, and then successively with cold water, alcohol, and ether; it is soluble in boiling dilute alcohol, but undergoes partial decomposition at the same time; it has a definite melting point, namely, 183°. The *osazone*, $C_{18}H_{22}N_4O_4$, can only be obtained free from the phenylhydrazone by repeated recrystallisation; it melts at 198°, crystallises in yellow needles, and is sparingly soluble in water or in cold alcohol, but dissolves readily in hot alcohol.

J. J. S.

Chemistry of Starch. By CARL J. LINTNER (*Chem. Zeit.*, 1897, **21**, 737—738 and 752—754).—The author points out the necessity of distinguishing between ordinary inversion dextrins, reversion dextrins, vegetable gums which are anhydrides of pentoses, and the products obtained by Zulkowski on heating starch with glycerol. All these groups of compounds are often spoken of as dextrins, but differ materially in their more important properties. General directions for the isolation of dextrins are given, and the paper concludes with an account of amylodextrin, erythrodextrin, achroodextrin and isomaltose. J. J. S.

Action of Diastase on Starch. By Hans Mittelmeier (*Chem. Centr.*, 1897, ii, 1010—1011; from *Mon. sci.*, [iv], 11, 2, 775—776. Compare Abstr., 1896, i, 336).—According to the author, the first stage of the action of diastase on starch results in the formation of equal amounts of two different amylodextrins, of which one is much more easily attacked by diastase than the other. Thus, while the one has only arrived at the erythrodextrin stage, the other has passed through all the stages from dextrin to sugar. On this hypothesis, the existence of a molecule of sugar and a molecule of dextrin in one molecular complex is intelligible. The author has prepared gelatinous osazones, and isolated an osazone which is apparently derived from an isomeride of maltose. E. W. W.

Gum-ammoniacum. By M. Frischmuth (*Chem. Centr.*, 1897, ii, 1078; from *Pharm. Zeit. Russ.*, **36**, 555—559).—The gum has the properties of a true carbohydrate, or, at least, contains true carbohydrate groups, the average rotatory power of the gum being $-32\cdot825°$, which is not affected by any acid or alkaline reaction of the liquid. When treated with hydrochloric acid of 20 per cent., it yields, besides humus matters, levulinic acid, and on oxidising with nitric acid of sp. gr. $= 1\cdot15$, it yields 31·3 per cent. of its weight of mucic acid (equivalent to 41·75 per cent. of galactose), but no saccharic acid. When distilled with dilute hydrochloric acid, it yields 9·35 per cent. of furfuraldehyde (equivalent to 16·67 per cent. of arabinose), and when boiled with dilute (1·25 per cent.) sulphuric acid, reducing sugars are obtained consisting chiefly of galactose. No cellulose could be detected. L. de K.

Synthesis of Organic Compounds by means of the Dark Electric Discharge. By Alexander de Hemptinne (*Chem. Centr.*, 1897, ii, 1044—1045; from *Bull. Acad. roy. Belg.*, [iii], **34**, 269—277).—The author finds that when mixtures of various gases are submitted to the action of the electric discharge in a Berthelot's ozoniser, the best results are usually obtained when the walls of the apparatus are near together; for each mixture, a certain definite distance is probably most advantageous. In the case of carbonic oxide and water vapour, the author has confirmed Losanitsch and Jovitschitsch's results (Abstr., 1897, i, 179); when the discharge passed through a distance of 7 mm. for 3 hours, the pressure was only reduced by 15 mm. of water, and only a little carbonic anhydride and formic acid were produced. With carbonic oxide and hydrogen, however, increasing the distance traversed by the discharge has apparently little effect on the formation of formaldehyde and its polymerides. Carbonic oxide and methane yield an aldehyde-like compound, and carbonic oxide and ethane, when cooled, form a ketone and a considerable quantity of aldehyde; both syntheses take place most readily when the walls of the ozoniser are not far apart. When a mixture of ethylic alcohol and oxygen is similarly treated, the best yield of acetic acid is obtained when the lower part of the apparatus is immersed in a freezing mixture, so that the acid which collects is solidified, and thus removed from the sphere of action. E. W. W.

Aldehyde-ammonia. By MARCEL DELÉPINE (*Compt. rend.*, 1897, **125**, 951—954).—*Ethylideneimine*, $CHMe\colon NH$ or $(CHMe\colon NH)_3$, obtained when aldehyde-ammonia is placed in a vacuum over sulphuric acid for several days, crystallises in brilliant, colourless crystals, melts at about 85°, boils at 123—124° under atmospheric pressure, has an odour resembling that of acetamide, and is soluble in water, alcohol, acetic acid, chloroform, benzene, or toluene; when its chloroform or benzene solution is allowed to evaporate spontaneously, the imine is obtained in the form of large, transparent crystals, resembling those of potassium bromide. Its molecular weight in benzene solution varies inversely with the concentration. Its vapour density at 261° agrees with the simple formula $CHMe\colon NH$, but at lower temperatures the vapour density is higher.

Heat of combustion at constant volume = 347·13 Cal.
" " " pressure = 347·6 "
" formation for $(CH_3CHNH)_3$ = 40·5 "

Determinations of the molecular weight of aldehyde-ammonia point to the formula $(C_2H_7NO)_3$. The vapour density at 182° indicates that decomposition into water and the simple imine has taken place.

Heat of combustion at constant volume = 346·54 Cal.
" " " pressure = 347·0 "

$C_2 + H_7 + N + O = C_2H_7NO$ cryst. + 83·1 Cal.
$C_2 + H_5 + N + H_2O$ liq. $= C_2H_7NO$ cryst. + 14·1 Cal.

The *picrate* of ethylideneimine is obtained when a saturated alcoholic solution of picric acid is added to an alcoholic solution of either aldehyde-ammonia or ethylideneimine; it crystallises in long, bright yellow needles, and is extremely readily soluble in water, but the solution readily decomposes into aldehyde and ammonium picrate.

J. J. S.

The Butyroins and Isovaleroin. By AUG. BASSE and HEINRICH KLINGER (*Ber.*, 1898, **31**, 1217—1225. Compare Abstr., 1891, 890).—The results of the following investigation confirm the view previously entertained by Klinger and Schmitz as to the constitution of the products obtained by the action of sodium on acid chlorides. This reaction does not appear to be a direct one, but is brought about by the presence of a small amount of water, the reduction being effected by the hydrogen liberated from this, and from the hydrogen chloride which is produced. Butyroin, as already described, is converted by aqueous potash into dipropylglycollic acid, melting at 78°, and yields an osazone, $N_2HPh\colon CPr^{a}\cdot CPr^{a}\colon N_2HPh$, which melts at 138°, and reacts in a similar manner to benzoin with carbamide and thiocarbamide. 4:5-*Dipropylglyoxaline 2-hydrosulphide*, $\begin{matrix} CPr^{a}\cdot NH \\ \| \\ CPr^{a}\text{——}N \end{matrix}\!\!>\!C\cdot SH$, obtained from thiocarbamide, crystallises in long, yellowish needles which do not melt below 290°. It has faintly acid properties, but its potassium salt is decomposed by water. *Dipropylacetylenemono-ureide*,

$$\begin{matrix} CPr^{a}\cdot NH \\ \| \\ CPr^{a}\cdot NH \end{matrix}\!\!>\!CO,$$

which is obtained from carbamide, crystallises in silky needles, which melt and decompose at 216°.

Isobutyroin, $COPr^{\beta}\cdot CHPr^{\beta}\cdot OH$, is prepared in a similar manner to the normal compound, and boils at 75—77° under a pressure of 12 mm. 4 : 5-*Di-isopropylglyoxaline 2-hydrosulphide* crystallises in hard, white needles, which do not melt below 290°, whilst the corresponding *di-isopropylacetylenemono-ureide* closely resembles it.

Isovaleroin boils at 80—105° under a pressure of 13 mm., and is converted by phenylhydrazine into *di-isovalerylosazone*, $C_{22}H_{30}N_4$, which crystallises in slender needles melting at 163°. 4 : 5-*Di-isobutylglyoxaline 2-hydrosulphide* crystallises in small, white needles, and is soluble in alkalis. *Di-isobutylacetylenemono-ureide* crystallises in slender, silky needles melting at 182—183°. *Isovaleroinoxime*, $C_4H_9\cdot C(NOH)\cdot CH(C_4H_9)\cdot OH$, forms lustrous plates melting at 128°. When isovaleroin is heated with aqueous potash in a current of air, it is partially converted into *di-isobutylglycollic acid*, which crystallises in soft needles melting at 119·5—120°. A. H.

Some Constituents of Wool Fat. By ERNST SCHULZE (*Ber.*, 1898, **31**, 1200—1202).—In view of the results obtained by Darmstädter and Lifschütz (this vol., i, 245) the author points out that he has confirmed the formula previously ascribed by him to isocholesterol, and further draws attention to the great variation which exists in the composition of different wool fats. A. H.

Constitution of Amidofumaric and Amidomaleic Derivatives. By RENE THOMAS-MAMERT (*Bull. Soc. Chim.*, 1897, [iii], **17**, 60—66).—Potassium amidofumaramate, obtained by treating amidofumaramide with the calculated amount of potassium hydroxide, may be either $NH_2\cdot CO\cdot C(NH_2)\colon CH\cdot COOK$ or $COOK\cdot C(NH_2)\colon CH\cdot CO\cdot NH_2$, but as, on reduction with aluminium amalgam in neutral solution, the potassium salt of isoasparagine, $NH_2\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot COOH$, and not that of the normal compound, $COOH\cdot CH(NH_2)\cdot CH_2\cdot CONH_2$, is obtained, the former formula must be adopted. The isoasparagine was identified by means of its copper salt, and was also separated in the free state. Since the ethylic amidofumaramate melting at 139·5°, obtained by the action of alcoholic ammonia on ethylic chlorofumaramate, also yields isoasparagine, it must be represented by the formula $NH_2\cdot CO\cdot C(NH_2)\colon CH\cdot COOEt$, and the chlorofumaramate by

$$NH_2\cdot CO\cdot CCl\colon CH\cdot COOEt.$$

The compound melting at 119·5°, isomeric with ethylic amidofumaramate, obtained by treating ethylic amidofumarate with aqueous ammonia, and thus apparently of the constitution

$$COOEt\cdot C(NH_2)\colon CH\cdot CO\cdot NH_2,$$

yields, however, isoasparagine on reduction, and since it differs considerably in its properties from the fumaric derivatives described, it is probably the stereoisomeric ethylic amidomaleamate. Attempts were made to determine the constitution of potassium ethylic amidofumarate by ascertaining which of the two ethylaspartic acids it yielded on reduction, but hydrolysis always occurred at some stage of the process, and inactive aspartic acid was obtained. Considering,

however, that ammonia is without action on the salt, and that in ethylic amidofumarate only the ethoxyl-group in the vicinity of the amido-group is attacked by ammonia, it appears most probable that potassium ethylic fumaramate is $COOK\cdot C(NH_2):CH\cdot COOEt$.

N. L.

The Tautomeric Forms of the Ethereal Salts of α-Ketonic Acids. By ROBERT SCHIFF (*Ber.*, 1898, 31, 1304—1306. Compare this vol., i, 355).—Since such salts are obtained by the condensing action of sodium ethoxide, they might be expected to have the enolic form, but it has not yet been possible to obtain the ketonic form. There is indirect evidence that they contain the group $C(OH)\cdot COOEt$; for not only do they give, in benzene solution, colorations with ethereal ferric chloride, but they resemble lactic acid, which also contains this group, in that they form compounds containing the group $C\!\left\langle{-O-}\atop{CO\cdot O}\right\rangle\!CH\cdot CCl_3$, when they are heated with excess of chloral hydrate at 100° or 150°.

Acetylpyruvic chloralide, $CHAc:C\!\left\langle{-O-}\atop{CO\cdot O}\right\rangle\!CH\cdot CCl_3$, melts at 137—138°; *benzoylpyruvic chloranilide* at 197—198°.

A sample of ethylic acetoacetate manufactured by the Höchst Colour Works, has been found to consist entirely of the enolic form, like the sample from Kahlbaum's described previously.

C. F. B.

Organic Urates Soluble in Water. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1897, 21, 544).—The urates of the following bases are soluble in hot water; namely, methylamine, benzylamine, nicotine, tetrahydroisoquinoline, and piperazine. The urates of piperidine, ethylamine, and propylamine are readily soluble in cold water.

J. J. S.

Constitution of Inorganic Compounds. XIV. Molecular Compounds of Tin Tetrahaloids with Tin Alkyls. By ALFRED WERNER and PAUL PFEIFFER (*Zeit. anorg. Chem.*, 1898, 17, 82—110).—Tindiethyl di-iodide was prepared according to Cahour's method, by heating ethylic iodide with tin foil in a sealed tube for 20 hours at 150°; it is most easily separated from the tintriethyl iodide, which is also formed, by dissolving it in methylic alcohol and precipitating with a small quantity of water. A determination of the molecular weight by Beckmann's boiling point method gave numbers agreeing with the formula $SnEt_2I_2$. Tindiethyl salts are most easily prepared from tindiethyl oxide, which is obtained by treating the iodide dissolved in alcohol with ammonia, is a white powder, and when treated with acids is converted into the corresponding salts. The chloride crystallises from light petroleum in silky needles, and melts at 84—85°. The bromide crystallises from light petroleum in prisms or tablets and melts at 63°. The sulphate crystallises from water in beautiful, quadratic crystals, does not melt when heated, and is not volatile with steam; the molecular weight determination gave numbers corresponding to half that required by the formula $SnEt_2SO_4$. The *phosphate*, $SnEt_2PO_4H$, crystallises from water in large, white

needles; it is soluble in water, and at first yields a clear solution, which, however, quickly becomes turbid and deposits a white powder containing phosphoric acid. Tindiethyl salts, when treated with ammonium carbonate, yield a white precipitate soluble in excess of ammonium carbonate, which is again precipitated by the addition of acid. With ammonium sulphide, a white precipitate is also obtained soluble in excess and again precipitated by hydrochloric acid. With hydrogen sulphide, a heavy oil is precipitated which has not been examined. According to the authors, compounds of the formula SnX_2Et_2 are capable of existing in stereoisomeric forms, and from stereochemical grounds tindiethyl sulphate can only exist in the cis-form, but the halogen compounds are probably of the trans-form, as this is the most stable; when, however, the sulphate is treated with barium iodide, the product is ordinary tindiethyl iodide. Tindiethyl salts are capable of forming molecular compounds only with ammonia and its substitution derivatives.

Tindiethyl chloride pyridine, $SnEt_2Cl_2,2C_5NH_5$, formed with evolution of heat when its constituents are mixed, crystallises from pyridine in transparent prisms, melts at 130°, gradually loses pyridine when exposed to the air, and may be crystallised without decomposition from absolute alcohol and light petroleum. The *bromide* crystallises in prisms or rhombic tablets and melts at 140° with decomposition. The *iodide* crystallises in white prisms, melts at 117°, is easily soluble in alcohol, and is much more readily decomposed than the chloride or bromide.

Tindiethyl chloride and iodide do not yield definite compounds with aniline; according to the length of time of the action of the aniline, the crystalline product varies in composition between the compounds $SnEt_2X_2,NH_2Ph$ and $SnEt_2X_2,2NH_2Ph$.

Tindiethyl chloride diammine, $SnEt_2Cl_2,2NH_3$, obtained by treating a solution of tindiethyl chloride in absolute ether with dry ammonia, is an amorphous, white powder insoluble in all the ordinary solvents and decomposes when heated, and when treated with water or potassium hydroxide. The *iodide*, $SnEt_2I_2,2NH_3$, is very similar to the chloride and gradually becomes yellow after a time.

Tintriethyl iodide and tintetrethyl are prepared according to Ladenburg's method, by the action of ethylic iodide on an alloy of tin and sodium containing 14 per cent. of sodium. The mixed product is separated by fractional distillation and the tintetrethyl finally separated from the small quantity of tintriethyl iodide, which it always contains, by dissolving it in absolute ether and treating the solution with dry ammonia, whereby the insoluble compound, $SnEt_3I,2NH_3$, is precipitated and the tintetrethyl is removed from the filtrate by distillation. Three molecular compounds of tintriethyl iodide are already known, namely $SnEt_3I,2NH_3$, $SnEt_3I,2NH_2\cdot C_5H_{11}$, and $SnEt_3I,2NH_2Ph$. The authors have examined the last compound, and find that it remains unaltered when crystallised either from aniline or alcohol, and therefore it contains the maximum number of aniline molecules; it crystallises in lustrous, white leaflets, and melts at 58°. The authors were unable to obtain a compound of tintriethyl

iodide with pyridine. Compounds with piperidine and dipropylamine are easily formed, but have not been examined.

Tintetrethyl does not form additive compounds; although the authors experimented with a large series of oxides, sulphides, and nitrides. Tintetraphenyl is also incapable of forming additive compounds; it is soluble in many organic bases and sulphides, and crystallises from all of them unchanged.

Leadtetraphenyl, prepared by the action of bromobenzene on lead sodium alloy, is separated from the diphenyl by treatment with alcohol, in which the diphenyl is easily soluble. It does not form additive compounds, and crystallises unchanged from dipropylamine and diethylic sulphide. When dissolved in chloroform and treated with a current of dry hydrogen chloride, it yields leaddiphenyl chloride.

Tin tetrachloride bisdimethylic sulphide, $SnCl_4,2SMe_2$, is obtained by the action of methyl sulphide on anhydrous tin chloride, the reaction being so violent that it is necessary to cool the mixture; it is a white, crystalline mass, very sparingly soluble in methylic sulphide, is decomposed at once by water, and gradually decomposes when allowed to remain even in a closed vessel. The *ethyl* compound, $SnCl_4,2SEt_2$, obtained in a similar manner to the preceding compound, crystallises from ethylic sulphide in large, white prisms, melts and decomposes at 101—102°, is easily soluble in alcohol and ether, and is decomposed by water with the formation of ethylic sulphide. The *amyl* compound, $SnCl_4,2S(C_5H_{11})_2$, is a white, crystalline mass, and melts and decomposes at 64°.

Tin tetrabromide bisdimethylic sulphide, $SnBr_4,2SMe_2$, is obtained as a crystalline mass and melts at 85—87°. It is remarkable for its intense yellow colour, although both its components are colourless; and as the colour is completely destroyed when it is decomposed by water, it is apparently characteristic of the compound, and is not due to decomposition products. The two following compounds have the same colour. The *ethyl* compound, $SnBr_4,2SEt_2$, crystallises from ethylic sulphide in large, transparent prisms, melts at 84°, is easily soluble in alcohol and ether, and is decomposed by water with the formation of ethylic sulphide. The *amyl* compound, $SnBr_4,2S(C_5H_{11})_2$, melts at 45—46°.

Tin tetrachloride pyridine, $SnCl_4,2C_5NH_5$, is formed from its components with evolution of a large amount of heat and forms an amorphous, white powder, which is insoluble in all the ordinary solvents; when heated it decomposes without melting and loses pyridine when boiled with methylic alcohol. The *tetrabromide pyridine*, $SnBr_4,2C_5NH_5$, is a white, amorphous mass resembling the tetrachloride, and decomposes on exposure to the air. The compounds of tin tetrachloride and tindiethyl chloride with pyridine both contain 2 molecules of pyridine to 1 molecule of tin haloid.

Although tin tetrahaloids form additive compounds with sulphides and pyridine, when treated with alcohols the additive compound is decomposed as soon as formed, hydrogen haloid is evolved, and compounds of the composition $SnCl_3\cdot OEt,EtOH$ are formed. When tin tetrachloride and absolute alcohol, both cooled to $-10°$, are mixed, a

white, crystalline powder is obtained. The compounds from tin tetrabromide and ethylic alcohol or amylic alcohol are similar.

E. C. R.

Furfurylsuccinic Acid. By S. S. Sandelin (*Ber.*, 1898, 31, 1119—1122).—Ethylic furfurylidenemalonate, $C_4OH_3\cdot CH\colon C(COOEt)_2$ (Marckwald, Abstr., 1888, 678), was converted into furfurylsuccinic acid by the method of Bredt and Kallen (Abstr., 1897, i, 154). The furfurylidenemalonate (1 mol.) in alcoholic solution was treated with potassium cyanide (2 mols.) in aqueous solution, the mixture boiled for 6 hours in a reflux apparatus, and the alcohol distilled off. It was not found possible to isolate pure cyano-β-furfurylpropionic acid, $C_4OH_3\cdot CH(CN)\cdot CH_2\cdot COOH$, from the residue; this residue was heated with aqueous potash until ammonia was no longer evolved, after which the solution was acidified, and the furfurylsuccinic acid extracted with ether.

Furfurylsuccinic acid, $C_4OH_3\cdot CH(COOH)\cdot CH_2\cdot COOH$, melts and decomposes at 154°; the *ethylic* salt boils at 199·5—200° under 79 mm. pressure, the *methylic* salt at 162—163° under 33 mm.; the *anil* melts at 152·5°. When the acid is heated under 67 mm. pressure, it evolves gas at 145°, and at 196—210° a substance distils which is nearly all β-furfurylpropionic acid, $C_4OH_3\cdot CH_2\cdot CH_2\cdot COOH$ (Baeyer, Abstr., 1877, 444), no anhydride being formed, as is the case with phenylsuccinic acid (Bredt and Kallen, *loc. cit.*). C. F. B.

Phenylic Iododichloride. By Ferd. Keppler (*Ber.*, 1898, 31, 1136—1137).—Phenylic iododichloride, $C_6H_5\cdot ICl_2$, cannot be kept in sealed tubes, even in the dark; it decomposes, forming parachloriodobenzene and hydrogen chloride. It remains unchanged, at any rate for two months, when it is placed in the bottom of an open desiccator with a dish of sulphuric acid over it, and the whole is kept in a dark place. C. F. B.

Formation of Acetylquinol from Acetaldehyde and Quinone in Sunlight. By Heinrich Klinger and Wilhelm Kolvenbach (*Ber.*, 1898, 31, 1214—1216. Compare Abstr., 1891, 900).—Acetaldehyde slowly combines with benzoquinone when exposed to sunlight, acetylquinol, $C_6H_3Ac(OH)_2$, being formed, which is identical with that described by Nencki and Schmid (*J. pr. Chem.*, 1881, 23, 547). The *monacetate*, $OAc\cdot C_6H_3Ac\cdot OH$, crystallises in broad, yellowish needles melting at 91°, and the *phenylhydrazone* of this compound crystallises in almost colourless needles and melts at 147°. The *diacetate* also forms needles and melts at 68°, whilst the *dibenzoate* crystallises in prisms melting at 113°, and yields a *phenylhydrazone* which crystallises in straw-coloured needles and melts at 148°.

A. H.

Oxide of Dichloromethoxyquinonedibenzoylmethylacetal. By C. Loring Jackson and H. A. Torrey (*Amer. Chem. J.*, 1898, 20, 395—430. Compare Abstr., 1897, i, 272).—When the oxide of dichloromethoxyquinonedibenzoylmethylacetal, previously called dichlorodimethoxyquinol dibenzoate, is treated with sodium hydroxide, it is

converted into sodium chloranilate; with sodium methoxide, it gives dichlorodimethoxyquinonedimethylhemiacetal.

Sodium methoxide acts on the ethyl oxide in a similar manner, the ethoxy-groups being replaced by methoxy-groups; the converse also being true, that when the methyl oxide is acted on by sodium ethoxide the methoxy- are replaced by ethoxy-groups.

Isoamylamine acts on the methyl oxide, giving an unstable, yellow substance, which, when heated, passes into the *isoamylamine salt of dichlorisoamylamidoxyquinone*, $C_5H_{11}\cdot NH\cdot C_6Cl_2O_2\cdot NH_2(OH)\cdot C_5H_{11}$; this crystallises from a mixture of benzene and methylic alcohol in purplish-red needles, and when heated decomposes into isoamylamine and *dichlorisoamylamidoxyquinone*; the latter can also be obtained by the action of hydrochloric acid on any of its salts; it forms bronze-black, flattened needles or long plates melting at 188°. The *silver* salt forms olive-grey needles containing $2H_2O$, which are lost on heating to 110°, the substance becoming red; and the barium *salt* consists of violet, crystalline plates.

Dichlorodi-isoamylamidoquinone, $(C_5H_{11}NH)_2C_6Cl_2O_2$, obtained by the action of isoamylamine on chloranil, or dichlorodimethoxyquinone, or dichlorodimethoxyquinonedimethyldibenzoylacetal, crystallises in long, dark red plates or flattened needles, often showing a marked purple iridescence when separating from solution, and melts at 224—225°.

Isoamylamine chloranilate, prepared by the action of the amine on chloranilic acid, is a purplish-red, crystalline substance. Di-isoamylamine acts on the oxide, giving rise to the *di-isoamylamine salt of dichlorodidi-isoamylamidoxyquinone*, which separates from light petroleum in reddish-brown crystals melting at 168—169°.

Dichlorodidi-isoamylamidoquinone, $C_6Cl_2O_2[N(C_5H_{11})_2]_2$, produced by the action of di-isoamylamine on chloranil, crystallises from alcohol in long, reddish-black needles; it is very unstable, readily giving off di-isoamylamine, and no accurate melting point could be taken.

Hydroxylamine is without action on the oxide, but phenylhydrazine gives a yellow substance, not further investigated.

Dichlorodimethoxyquinonedimethyldiacetylacetal, prepared by the action of acetic chloride on the sodium salt of dichlorodimethoxyquinonedimethylhemiacetal, crystallises from a mixture of chloroform and alcohol in white, monclinic prisms or rhombic plates melting at 177—178°. When heated with sulphuric acid, only chloranilic acid could be isolated, and not an oxide similar to the one obtained from the benzoylacetal. The corresponding *diethyl* derivative crystallises in very sharp, rhombic plates with bevelled edges, and melts at 120—121°.

With the hope of ascertaining whether the atom of oxygen in the oxide is in the ortho- or meta-position, the authors have studied the action of sulphuric acid on certain dihydric phenols. Without obtaining any definite evidence, they believe it has the ortho-attachment.

Tetrabromoguaiacol, $OMe\cdot C_6Br_4\cdot OH$, obtained by the action of bromine on guaiacol, crystallises from chloroform in long, white, slender prisms or thick needles melting at 162—163°. When treated

with concentrated nitric acid in glacial acetic acid solution, a red substance is formed, probably tetrabromorthoquinone.

Tribromoveratrole, $C_6HBr_3(OMe)_2$, prepared by the action of methylic iodide on tribromoguaiacol, crystallises from hot alcohol in slender, white needles melting at 86—87°. With concentrated nitric acid, it also yields a red substance, probably tribromorthoquinone.

The action of sodium alkyloxides on some substituted quinones was begun by the authors, but given up on account of Astre's work (Abstr., 1896, i, 18, 153) in a similar direction; they cannot, however, agree with Astre's formulæ for the substances produced, in which sodium is supposed to have replaced hydrogen attached to the benzene ring.

When sodium chloranilate is treated with iodine and sodium hydroxide, iodoform is produced. A. W. C.

Action of Acetic Anhydride on Quinone and on Dibenzoylstyrene. By Johannes Thiele (*Ber.*, 1898, 31, 1247—1249).—When quinone (150 grams) is added in small quantities to acetic anhydride (400—450 grams) containing concentrated sulphuric acid (10 c.c.), it rapidly dissolves, and the liquid becomes hot; after maintaining the temperature at 40—50° until all the quinone is added, the solution is poured into much water, when the triacetyl derivative of hydroxyquinol separates; this melts at 96·5—97°, and is identical with the compound described by Barth and Schreder; the yield obtained by this method represents 80 per cent. of that required by theory. The substance forms a colourless solution in concentrated sulphuric acid, dilution with a small quantity of water developing a pink coloration, which is destroyed on further addition of the diluent. The acetate distils considerably above 300° without undergoing decomposition; it is very readily hydrolysed by acids and alkalis.

Acetyltriphenylfurfuranol, $\begin{matrix}C(OAc){:}CPh \\ | \\ CPh{=\!=}CPh\end{matrix}\!\!>\!O$, is obtained by suspending dibenzoylcinnamene, $CPh\cdot C(COPh){:}CH(COPh)$, in acetic anhydride, and treating it with a small quantity of concentrated sulphuric acid; it crystallises from alcohol in long, lustrous prisms, and melts at 135°. A minute quantity of the substance develops a beautiful, bright green fluorescence with concentrated sulphuric acid.

A mixture of acetic anhydride and concentrated sulphuric acid converts the two naphthaquinones into the same triacetyl derivative of 1 : 2 : 4-trihydroxynaphthalene; terephthalaldehyde yields the tetracetyl derivative, $C_6H_4[CH(OAc)_2]_2$. M. O. F.

Characteristic Reaction of Orthophenols: Derivatives of Antimonylcatechol. By Henri Causse (*Compt. rend.*, 1897, 125, 954—956). Compare Abstr., 1893, i, 75).—The property, which all orthophenols possess, of forming antimonyl derivatives, similar to those previously described in the case of catechol and pyrogallol, serves as the basis of a method for separating them from their isomerides. Certain other phenols also form somewhat similar derivatives, but the latter are amorphous, are readily dissociated by cold alcohol, and do not yield halogen derivatives, &c. The best method of separating

the antimonyl derivatives is by the aid of dilute halogen hydracids; the derivative of the ortho-compound crystallises out, and all other derivatives are decomposed.

Antimonylcatechol chloride, $C_6H_4<^O_O>SbCl$, is best obtained by the action of an aqueous solution of antimony chloride on catechol; it often contains a quantity of the hydroxy-compound, from which it can be freed by solution in hydrochloric acid, diluting, and then boiling; when cold, the chloride crystallises in plates which are insoluble in the usual solvents.

The *bromide*, $C_6H_4O_2SbBr$, may be obtained in a similar manner, or more readily by dissolving the hydroxide in hydrobromic acid.

The *iodide* is best obtained by diluting 50 c.c. of a 50 per cent. solution of hydriodic acid with 3—4 times its volume of water, saturating with potassium iodide, then with oxide of antimony, and finally adding 25 grams of catechol; the solution is then poured into a solution of catechol (25 grams) in water (50 grams), previously heated to 40—50°, when the iodide crystallises out.

The *fluoride*, $C_6H_4O_2SbF$, and *oxalate*, $C_6H_4O_2Sb{\cdot}C_2HO_4$, are also described; the latter is best obtained by adding a hydrochloric acid solution of the chloride to a boiling solution of potassium hydrogen oxalate. J. J. S.

Composition of Wool Fat, VI. The Cholesterols of Wool Fat. By L. Darmstaedter and Isaac Lifschütz (*Ber.*, 1898, 31, 1122—1127. Compare this vol., i, 245).—When the half-liquid Fraction 2, obtained in the separation of the alcohols of the soft fat by means of methylic alcohol, is dissolved in 2—3 volumes of ether and allowed to remain at 0°, small, white needles of a substance, Alcohol 2a, separate; these melt at 76—77°, and solidify at 70—72°. When the ether is evaporated from the filtrate and the residue is diluted largely with light petroleum, flakes remain undissolved; these dry to a resinous substance, designated Alcohol 2b. The filtrate from this, after evaporation of the petroleum, leaves a neutral, yellow, viscid liquid free from inorganic constituents: Alcohol 2c.

When a small quantity of Alcohol 2c is dissolved in glacial acetic acid, and a little strong sulphuric acid is added, the solution turns pale reddish-yellow, without becoming hot, and then becomes green, when its absorption spectrum shows a pronounced narrow band between C and d, and a less pronounced one at D. Neither cholesterol nor isocholesterol behave like this. If, however, the solution is diluted with an equal volume of acetic anhydride, it becomes warm, and after an hour the absorption bands of cholestol and isocholesterol can be observed. When the alcohol is heated with 2—3 parts of benzoic anhydride on the water bath, it yields an amorphous, soft, buttery benzoate, soluble in acetic acid; from this, the alcohol can be regenerated by hydrolysis with alcoholic potash. In addition, a mixture of two crystalline benzoates, insoluble in acetic acid, is obtained; this yields, when hydrolysed, a mixture of about 2 parts of cholesterol with 1 of isocholesterol. Probably Alcohol 2c is a sort of hydrated cholesterol. Cholesterol

can be converted into it, to the extent of 20—25 per cent., by boiling with alcoholic potash of double normal strength.

When a solution of isocholesterol in acetic anhydride is heated to boiling with a drop of strong sulphuric acid, the solution turns green, and shows the absorption bands of cholesterol. If the boiling is continued until the solution has acquired a permanent violet-red tint, and the cooled solution is diluted with absolute alcohol, the green, alcoholic solution shows the bands of both isocholesterol and cholesterol, and the small, insoluble residue gives Liebermann's cholestol reaction with acetic anhydride and a drop of sulphuric acid, just as cholesterol does.

The following amounts of different substances have been obtained from 100 parts of the alcohols of the soft fat: Alcohol 2c, 50—54; isocholesterol, 11; Alcohol 2a, 3—4; Alcohol 2b, 6—7; non-cholesterols, not yet investigated, 24—30. C. F. B.

Chemical Activity of Organic Ammonium Salts. By JULIUS TAFEL (*Ber.*, 1898, **31**, 1152—1154).—The following experiments were undertaken to investigate the action of reagents on certain groups, when present in an ion of an electrolyte, and for this purpose the quaternary ammonium salts were chosen. Phenyltrimethylammonium hydrochloride and hydrobromide are not acted on in aqueous solution by chlorine or bromine, which are not electrolytes. The salts of aniline, on the other hand, and those of methylaniline and dimethylaniline, are readily converted into halogen derivatives in this way, and this may be due to the fact that the salts of these bases readily dissociate in solution into the free base and acid. Phenyltrimethylammonium nitrate, however, is readily converted by nitric acid, which is an electrolyte, into *mononitrophenyltrimethylammonium nitrate*, which crystallises in long, yellow prisms. Triethylallylammonium bromide combines very readily with bromine in aqueous solution to form a *perbromide*, which loses bromine on exposure to the air, yielding *triethyldibromopropylammonium tribromide*, $C_3H_5Br_2 \cdot NEt_3Br_3$, crystallising in colourless, silky plates. When the solution of this substance in acetone is heated, bromine is removed, with formation of *triethyldibromopropylammonium bromide*, $C_3H_5Br_2 \cdot NEt_3Br$, which crystallises in colourless, silky plates. A. H.

Action of Orthoxylylenic Bromide on Primary Aromatic Amines. By MAX SCHOLTZ (*Ber.*, 1898, **31**, 1154—1158. Compare this vol., i, 305, 383).—When heated with orthoxylylenic bromide, orthochloraniline yields *xylylenebisorthochloraniline*,

$$C_6H_4(CH_2 \cdot NH \cdot C_6H_4Cl)_2,$$

which crystallises in colourless plates melting at 79°; whilst the corresponding *xylylenebisorthobromaniline* crystallises in white plates melting at 132°. Orthanisidine and α-naphthylamine only react with one bromine atom of the dibromide in chloroform solution in the cold, but when the substances are heated together in alcoholic solution, complete reaction takes place. *Xylylenebisorthanisidine*,

$$C_6H_4(CH_2 \cdot NH \cdot C_6H_4 \cdot OMe)_2,$$

crystallises in long, delicate needles melting at 105°, whilst *xylylene-*

bis-a-naphthylamine melts at 148°. β-Naphthylamine, on the other hand, yields 2′-β-*naphthyldihydroisoindole*, $C_6H_4<{CH_2 \atop CH_2}>N\cdot C_{10}H_7$, which crystallises in colourless plates melting at 232°. This shows that the second ring of the naphthalene molecule acts in the same way as a group in the ortho-position to the amido-group. The presence of two ortho-groups appears to hinder the reaction more powerfully than a single group, for mesidine, $C_6H_2Me_3\cdot NH_2$ [$Me_3 : NH_2 = 1:3:5:6$], does not yield any compound analogous to those formed by ortho-amines; whilst the isomeric pseudocumidine [$Me_3 : NH_2 = 1:3:4:6$] undergoes the normal reaction. Orthomethylbenzylamine, $C_6H_4Me\cdot CH_2\cdot NH_2$, in which the amido-group is not combined with a carbon atom of the ring, acts like a meta- or para-compound, and yields *orthomethylbenzyldihydroisoindole*, $C_6H_4<{CH_2 \atop CH_2}>N\cdot CH_2\cdot C_6H_4Me$, which has not been obtained in the solid form, but yields a crystalline *hydrochloride*.

A. H.

Some Perhaloids. By A. Samtleben (*Ber.*, 1898, **31**, 1141—1148).—A number of perhaloid compounds, NR_2R', HX, X_2, have been prepared by adding either a hydrochloric acid solution of iodine chloride, bromine, or a solution of iodine in potassium iodide to a solution of a salt of a mixed aliphatic-aromatic tertiary amine at 0°. With the exception of the periodides, these compounds are decomposed by water, and still more readily by alkalis, pariodo- or parabromo-derivatives being formed; should the para- (or even, in the case of dimethyl- and diethyl-toluidine, the ortho-) position be occupied, either the original amine is regenerated, or resinous products are formed. The numbers quoted below are melting (or decomposing) points.

Dimethylaniline hydrochloride chloriodide, NMe_2Ph,HCl,ICl, yellow, 77°. *Diethylaniline hydrochloride chloriodide*, an oil; *pariododiethylaniline*, 32°. *Parabromodimethylaniline hydrochloride chloriodide*, $C_6H_4Br\cdot NMe_2,HCl,ICl$, yellow, 113°. *Tetramethyldiamidobenzophenone hydrochloride chloriodide*, $CO(C_6H_4\cdot NMe_2,HCl,ICl)_2$, yellow, 76°. *Nitrosodimethylaniline hydrochloride chloriodide*, $NO\cdot C_6H_4\cdot NMe_2,HCl,ICl$, yellow, 164°. *Diethylaniline hydrobromide perbromide*, NEt_2Ph,HBr,Br_2, orange-red, 81°. *Diethylorthotoluidine hydriodide periodide*,

$$C_6H_4Me\cdot NEt_2,HI,I_2,$$

steel-blue to dark brown, 100°. *Parabromodimethylaniline hydriodide periodide*, brownish-red, 124—125°.

Phenyltrimethylammonium iodide and iodine chloride yield a mixture of phenyltrimethylammonium periodide, NMe_3PhI,I_2, and *chloridechloriodide*, NMe_3PhCl,ICl, yellow, 118°.

4-*Hydroxytetramethylpiperidine hydrobromide perbromide*,

$$OH\cdot CH<{CH_2\cdot CMe_2 \atop CH_2\cdot CMe_2}>NH,HBr,Br_2,$$

red, 160°, yields *bromo-4-hydroxytetramethylpiperidine*,

$$OH\cdot CH<{CH_2\cdot CMe_2 \atop CH_2\cdot CMe_2}>NBr,$$

yellow, 101°, when it is treated with aqueous alkalis. The latter

substance is also obtained by the action of bromine on the free base. 1 : 2 : 2 : 6 : 6-*Pentamethylpiperidine hydrobromide perbromide*, 145°.

C. F. B.

Reaction of Diazo-salts with Phenols. By CHARLES GASSMANN and HENRY GEORGE (*Compt. rend.*, 1897, **125**, 306—309).—The authors have come to the conclusion that all phenols and naphthols, which, when united with a diazo-salt, yield orthohydroxy-derivatives, can react with such diazo-salts in neutral or even acid solutions. Several examples are given.

A 15 per cent. solution of β-naphthol in triacetin is recommended as a reagent suitable for titrating diazo-solutions; it is preferable to the usual reagent, namely, sodium 2-naphthol-3 : 3′-disulphonate.

It has been noticed that, as a rule, nitrated diazo-salts react with phenols more readily than do simple diazo-salts. Two different dyes may be obtained from orthonitrobenzidine by diazotising, and then combining it with salicylic acid and 1-naphthol-4-sulphonic acid; the product varies according to the order in which the latter reagents are employed. The constitution of these two dyes is explained by the generalisation regarding nitrated derivatives given above.

J. J. S.

Halogenised Diazonium Thiocyanates, and their Rearrangement into Thiocyanodiazonium Salts. By BENNO HIRSCH (*Ber.*, 1898, **31**, 1253—1268. Compare Hantzsch and Hirsch, Abstr., 1896, i, 428).—*Parabromobenzenediazonium thiocyanate* is prepared from parabromobenzenediazonium chloride and potassium thiocyanate in absolute alcohol at 0°, and separates, on adding absolute ether, in the form of a reddish resin, which becomes yellow and solid when rubbed with a glass rod; it is sparingly soluble in absolute alcohol, but is very hygroscopic, and when freshly prepared dissolves readily in water.

Parathiocyanobenzenediazonium bromide, $NCS{\cdot}C_6H_4{\cdot}NBr{\vdots}N$, is obtained on extracting the foregoing compound with spirit, and filtering into common ether; it is more conveniently prepared by allowing the ice-cold solution of freshly-prepared parabromobenzenediazonium chloride to remain at the ordinary temperature for 8—10 minutes after filtration from the potassium chloride, when ether precipitates the thiocyanodiazonium salt. Free hydrochloric acid also exerts a favourable influence in the rearrangement of parabromobenzenediazonium thiocyanate. The compound obtained in the manner described is almost white, those diazonium bromides which have been hitherto prepared being intensely yellow; it dissolves with some difficulty in ordinary alcohol, and remains unchanged in the desiccator. It explodes with great violence at about 94°.

Orthochlorobenzenediazonium thiocyanate is a dark yellow compound which explodes at 46°. *Orthothiocyanobenzenediazonium chloride* explodes at 105°.

Metachlorobenzenediazonium thiocyanate forms yellow needles, and explodes with great violence in air; when preserved in a desiccator of brown glass, it quickly disappears, filling the vessel with vapour.

It has not been converted into metathiocyanobenzenediazonium chloride.

3 : 5-*Dibromoparatoluenediazonium thiocyanate*, [$Me : Br_2 = 1 : 3 : 5$], is an orange, crystalline substance, which decomposes without explosion at 40—50°. It yields two products of rearrangement, which probably have the composition expressed by the formulæ

$$NCS{\cdot}C_6H_2MeBr{\cdot}N_2{\cdot}NCS$$

and $NCS{\cdot}C_6H_2MeBr{\cdot}N_2{\cdot}Br$ respectively.

Trithiocyanobenzenediazonium thiocyanate, $(NCS)_3C_6H_2{\cdot}N_2{\cdot}NCS$, is prepared by treating tribromobenzenediazonium sulphate with excess of potassium thiocyanate, tribromobenzenediazonium thiocyanate (*loc. cit.*) being produced when the calculated quantity is employed; it is an intensely yellow, amorphous substance, inexplosive at ordinary temperatures, and detonating at 79—80°. It is very sparingly soluble in water, and, after a long interval, develops a blood-red coloration with a dilute solution of ferric chloride. Boiling water liberates hydrothiocyanic acid, whilst cold acetone and aniline eliminate nitrogen; when the latter substance is employed, detonation occurs.

M. O. F.

Rearrangement of Benzylidenephenylhydrazone. By JOHANNES THIELE and ROBERT H. PICKARD (*Ber.*, 1898, 31, 1249—1251).—*β-Benzylidenephenylhydrazone* is obtained when the ordinary phenylhydrazone of benzaldehyde, suspended in 4 parts of acetic anhydride, is cooled with ice and treated with a further quantity of the anhydride containing a small proportion of zinc chloride or concentrated sulphuric acid; when dissolution is complete, water is added, and the colourless product crystallised from a small quantity of glacial acetic acid; it forms small, white needles, and melts at 136°.

The new phenylhydrazone is readily soluble in organic solvents excepting petroleum, and dissolves more freely than the α-compound. It is very labile, changing completely into the isomeride when exposed in the desiccator during about a week; the same alteration takes place in a few hours when the substance is heated in a toluene bath, and in a still shorter period (30 minutes) when the solution in alcohol is treated with a few drops of alcoholic potash.

β-Benzylidenephenylhydrazone gives Bülow's reaction, and yields the dibenzylidenediphenylhydrotetrazone obtained from α-benzylidenephenylhydrazone and amylic nitrite (compare Abstr., 1895, i, 74); it does not, however, give rise to the compound (m. p. 202°) isolated by Ingle and Mann (Trans., 1895, 606). With iodine in presence of sodium ethoxide, it yields exclusively *syn*-benzileosazone, whilst α-benzylidenephenylhydrazone gives rise to dibenzylidenedihydrotetrazone along with this product. When lead peroxide is added to a solution of the α-phenylhydrazone in glacial acetic acid, dibenzylidenedihydrotetrazone is precipitated, a portion of the phenylhydrazone remaining dissolved; the β-compound, however, gives no precipitate, but on adding water and extracting the product with benzene, alcohol precipitates a small quantity of *anti*-benzileosazone.

In view of the behaviour of the two modifications of benzylidene-

phenylhydrazone, the authors regard them as stereoisomerides, representing the α-compound by the formula $\begin{array}{l}C_6H_5\cdot CH\\ \quad\quad\;\; \| \\ \quad\quad\;\; N\cdot NH\cdot C_6H_5\end{array}$, its relation to the β-compound being indicated by the expression $\begin{array}{r}C_6H_5\cdot CH\\ \| \\ C_6H_5\cdot NH\cdot N\end{array}$, for the latter substance.

Benzophenonephenylhydrazone and the phenylhydrazone of phenyl paratolyl ketone are indifferent to the action of acetic anhydride containing concentrated sulphuric acid. M. O. F.

Bromination of Alkylated Phthalimides: Derivatives of Methylphthalimide. By Franz Sachs (*Ber.*, 1898, 31, 1225—1233).—The most convenient method of preparing alkyl derivatives of phthalimide is by distilling the phthalate of the corresponding amine; this process giving more satisfactory results than treatment of potassium phthalimide with an alkylic iodide. Determinations in which the thermometer thread was completely surrounded with the vapour of the boiling substance show that the methyl, ethyl, propyl, isopropyl, and butyl derivatives of phthalimide boil at 285·7° (761 mm.), 285·0° (758 mm.), 296·9° (758 mm.), 286·0° (761 mm.), and 311·8° (758 mm.) respectively.

Bromomethylphthalimide, $C_6H_4<\substack{CO\\CO}>N\cdot CH_2Br$, obtained by the action of bromine on methylphthalimide at 160—170° during 5—8 hours, crystallises from chloroform or benzene in rhombic prisms, and melts at 149—150°. The substance produces an irritating effect on the mucous membrane. When heated with hydrobromic acid, it yields phthalic acid, ammonium bromide, and formaldehyde.

Methoxymethylphthalimide, $C_6H_4<\substack{CO\\CO}>N\cdot CH_2\cdot OMe$, prepared by heating a solution of bromomethylphthalimide in methylic alcohol with finely powdered potassium cyanide, crystallises from hot alcohol in colourless needles, and melts at 120—121°. *Ethoxymethylphthalimide* formed on heating bromomethylphthalimide dissolved in absolute alcohol with potassium iodide, and also produced when an attempt is made to recrystallise crude bromomethylphthalimide from alcohol, crystallises from petroleum or benzene in long needles, and melts at 83°, boiling at 325° (corr.) under atmospheric pressure.

Hydroxymethylphthalimide, $C_6H_4<\substack{CO\\CO}>N\cdot CH_2\cdot OH$, is obtained when bromomethylphthalimide is dissolved in boiling water, from which it separates in crystals containing water of crystallisation; when recrystallised from toluene, it melts at 141—142°, decomposing at 184° with elimination of formaldehyde; it has a feeble, bitter taste. The *hydriodide* crystallises from chloroform in large, robust, monoclinic prisms, and melts at 148—150°; it is insoluble in warm water, but dissolves in hot alcohol, which eliminates hydrogen iodide, and regenerates the ethoxy-derivative.

Diphthalimidodimethyl ether, $(C_6H_4<\substack{CO\\CO}>N\cdot CH_2)_2O$, is prepared by

dissolving hydroxymethylphthalimide in 5—10 parts of warm phosphorus oxychloride, which is boiled during a very short period, and then rapidly cooled; it crystallises from ethylic acetate in short, snow-white prisms, and melts at 207°.

Chloromethylphthalimide, $C_6H_4<\substack{CO\\CO}>N\cdot CH_2Cl$, produced when the solution of hydroxymethylphthalimide in phosphorus oxychloride is boiled during half an hour, is insoluble in water and petroleum, dissolving with difficulty in ether, but crystallises from benzene, and melts at 132—133°.

Tribromethylphthalimide, $C_6H_4<\substack{CO\\CO}>N\cdot C_2H_2Br_3$, is obtained by the direct action of bromine on ethylphthalimide and on bromethylphthalimide, and after crystallisation from chloroform melts at 190—191°. Concentrated hydrobromic acid resolves the substance into phthalic acid, ammonia, hydrogen bromide, and bromacetic acid.

M. O. F.

Synthesis of a Phosphazine. By WILHELM AUTENRIETH and OTTO HILDEBRAND (*Ber.*, 1898, 31, 1111—1113).—Phenoxythiophosphodiamide (this vol., i, 419) will not condense with benzile, but phenoxythiophosphoric dichloride, $OPh\cdot PSCl_2$ (*ibid.*), will condense with orthophenylenediamine when it (1 mol.) is first boiled with that substance (2 mols.) in ethereal solution in a reflux apparatus, the solution evaporated on the water bath, and the residue heated at 150—170° until it is quite solid and dark violet in colour. From this P-*thiophenoxyphenophosphazine*, $OPh\cdot PS<\substack{NH\\NH}>C_6H_4$, is obtained by extraction with ether; probably an intermediate product is formed by the reaction of one only of the two chlorine atoms. The phosphazine melts at 185°, and is a neutral, stable substance; neither aqueous alkalis nor mineral acids decompose it; prolonged boiling with alcoholic potash or strong hydrochloric acid does effect a decomposition, however.

C. F. B.

Synthesis of Aromatic Aldehydes. By LUDWIG GATTERMANN [and C. FRENZEL] (*Ber.*, 1898, 31, 1149—1152. Compare Abstr., 1897, i, 519).—Aldehydes cannot be prepared from the phenolic ethers by the method previously described, because the cuprous chloride which is necessary does not dissolve in the ethers in presence of aluminium chloride. Such aldehydes can, however, be readily obtained, and in almost theoretical amount, by the action of hydrocyanic acid and hydrogen chloride on the ether in presence of aluminium chloride. Orthotolylic methylic ether is thus first converted into the *imide*, $OMe\cdot C_6H_4\cdot CH\!:\!NH$, the *hydrochloride* of which forms white crystals and is very unstable, decomposing when warmed with water, acids, or alkalis into ammonium chloride and the free aldehyde, $OMe\cdot C_6H_4\cdot CHO$. This compound is a colourless oil, boils at 251° and is converted by oxidation into the acid, $OMe\cdot C_6H_4\cdot COOH$, melting at 192°, the constitution of which is known.

The following aldehydes have also been prepared, the yield being in

every case at least 80 per cent. of the theoretical. Methoxytolualdehyde [Me : CHO : OEt = 1 : 3 : 6] boils at 258—260°, whilst the *isomeride* [Me : CHO : OEt = 1 : 2 : 5] boils at 257°, and the third *isomeride* [Me : CHO : OEt = 1 : 3 : 4] boils at 250°. *Methoxychlorobenzaldehyde* [CHO : Cl : OMe : 1 : 3 : 4], from orthochloranisoil, boils at 53°, and *dimethoxybenzaldehyde*, $C_6H_3(OMe)_2 \cdot CHO$ [2 : 4 : 1], from resorcinol dimethylic ether, melts at 71°. A. H.

Double Compounds of Aromatic Ketones with Orthophosphoric Acid. By AUGUST KLAGES and PAUL ALLENDORF (*Ber.*, 1898, 31, 1298—1301).—When an excess of a ketone is mixed with orthophosphoric acid (originally crystalline, but fused and then overcooled), or with the syrupy acid, crystals of a double compound, $R \cdot CMeO,H_3PO_4$, are formed. Those compounds are stable in the presence of ether, and can even be crystallised from that solvent; they are decomposed by water or alcohol, and when distilled, or allowed to remain in the air, they lose the ketone. Benzophenone does not form such a compound, nor do those ketones in which the two ortho-positions relatively to the CMeO group are occupied by methyl groups; namely, acetylmesitylene, diacetylmesitylene, acetyldurene, diacetyldurene and acetylisodurene. Compounds were prepared with the following ketones; their melting points are quoted.

Acetophenone, 88—90°; *acetylparaxylene*, 82—83°; *acetylpseudocumene*, 132—133°; *acetylthienone*, 92—96°. C. F. B.

Action of Halogenated Acid Chlorides on Benzene in Presence of Aluminium Chloride. By A. COLLET (*Bull. Soc. Chim.*, 1897, [iii], 17, 66—80. Compare Abstr., 1897, i, 344 and 522).—Examination of the behaviour of a number of halogenated acid chlorides, when treated with benzene in presence of aluminium chloride, shows that, however the experimental conditions may be varied, only the chlorine atom attached to the carbonyl group enters into reaction, the corresponding simple halogenated ketones being produced. In this respect they differ from the chlorinated acetic chlorides, in which the whole of the chlorine may, under certain conditions, be replaced by the phenyl group. Phenyl bromomethyl ketone, $CH_2Br \cdot COPh$, from bromacetic chloride and benzene, is identical with the compound obtained by bromination of phenyl methyl ketone.

Phenyl α-bromethyl ketone, $CHMeBr \cdot COPh$, from α-bromopropionic chloride, is a colourless, highly refractive oil, boiling and decomposing at 245—250° and having a sp. gr. = 1·439 at 0°. It is insoluble in water, but miscible with most organic solvents. Potassium permanganate in alkaline solution oxidises it to benzoic acid; alcoholic ammonia converts it into diphenyldimethylparadiazine, $C_4N_2Me_2Ph_2$; and with hydroxylamine it yields phenylmethylglyoxime,

$$NOH{:}CMe \cdot CPh \cdot NOH.$$

With aromatic amines in the cold or at 100°, various "anilides" are obtained, whilst at higher temperatures derivatives of indole are produced. *Phenyl anilidoethyl ketone*, $NHPh \cdot C_2H_4 \cdot COPh$, crystallises in yellow

needles melting at 98°, and forms well-defined salts. Treated with acetic anhydride or chloride, it yields an *acetyl* derivative,

$$NPhAc\cdot C_2H_4\cdot COPh,$$

melting at 55°, whilst with benzoic chloride the corresponding *benzoyl* derivative, $NPhBz\cdot C_2H_4\cdot COPh$, melting at 103—104°, is produced. A *nitroso*-derivative, $NO\cdot NPh\cdot C_2H_4\cdot COPh$, melting at 75°, was also prepared. *Phenyl methylanilidoethyl ketone*, $NPhMe\cdot C_2H_4\cdot COPh$, melts at 48°; the *orthotoluidide*, $C_6H_4Me\cdot NH\cdot C_2H_4\cdot COPh$, at 89—90°; the *paratoluidide* at 90—91°; the *metaxylidide*, $C_6H_3Me_2\cdot NH\cdot C_2H_4\cdot COPh$ [NH : Me : Me = 4 : 1 : 3], at 161—161·5°; the *α-naphthalide*,

$$C_{10}H_7\cdot NH\cdot C_2H_4\cdot COPh,$$

at 161—163°; and the *β-naphthalide* at 120—121°. *2′:3′-Phenylmethylindole*, $C_6H_4<^{CMe}_{NH}>CPh$, and *2′-phenyl-1:3′-dimethylindole*,

$$C_6H_3Me<^{CMe}_{NH}>CPh,$$

are colourless, crystalline substances melting at 91—92° and 92—94° respectively. Most of the compounds just described have also been prepared from the phenyl bromethyl ketone obtained by direct bromination of phenyl ethyl ketone, which is therefore identical with the bromo-ketone produced from α-bromopropionic chloride.

The product of the action of α-bromobutyric chloride on benzene is the phenyl bromopropyl ketone, $CHEtBr\cdot COPh$, which has already been described (*loc. cit.*). It is converted by alcoholic ammonia into *diphenyldiethylparadiazine* melting at 140°, and by hydroxylamine into phenylethylglyoxime melting at 204—206°. The following new derivatives of phenyl propyl ketone have been prepared; the *metaxylidide*, $C_6H_3Me_2\cdot NH\cdot CHEt\cdot COPh$, melting at 106—107°; the *α-naphthalide*, $C_{10}H_7\cdot NH\cdot CHEt\cdot COPh$, melting at 137—138°; and the *β-naphthalide*, melting at 151—152°.

From α-bromisobutyric chloride and benzene, a yellowish liquid of disagreeable odour was obtained, which proved to be impure *phenyl α-bromisopropyl ketone*, $CMe_2Br\cdot COPh$. Phenyl isopropyl ketone, when brominated directly, yields an oily liquid of sp. gr. = 1·379 at 0° which gives benzoic acid on oxidation with alkaline permanganate, and forms an *anilido*-derivative melting at 136—137°. It is therefore either $CH_2Br\cdot CHMe\cdot COPh$ or $CMe_2Br\cdot COPh$.

Phenyl β-chlorethyl ketone, $CH_2Cl\cdot CH_2\cdot COPh$, from β-chloropropionic chloride and benzene, was not obtained sufficiently pure for analysis. It forms an *aniline* derivative melting at 111—112°.

N. L.

Brominated Ketones. By A. Collet (*Compt. rend.*, 1897, **125**, 305—306 Compare this vol., i, 139).—*Paratolyl α-bromethyl ketone*, $C_6H_4Me\cdot CO\cdot CHBrMe$, is obtained by gradually adding aluminium chloride (70 grams) to a mixture of α-bromopropionic chloride (50 grams) and toluene (200 grams) at the ordinary temperature; the product is poured into cold water, the toluene layer decanted and distilled, first at atmospheric pressure to remove the toluene, and later under diminished pressure, when the ketone passes over at 160—162° under

20 mm. pressure. It crystallises from boiling alcohol in small plates melting at 76—77°, is soluble in alcohol, benzene or toluene, and when oxidised with alkaline potassium permanganate yields terephthalic acid; it reacts with an alcoholic solution of aniline, yielding paratolyl anilidoethyl ketone, $C_6H_4Me\cdot CO\cdot CHMe\cdot NHPh$, crystallising in yellow needles and melting at 104—105°.

Paratolyl α-bromopropyl ketone, $C_6H_4Me\cdot CO\cdot CHBrEt$, a yellow oil with a disagreeable odour, distils at 169—173° under 20—25 mm. pressure, and decomposes when heated at atmospheric pressure.

Paraxylyl α-bromethyl ketone, $C_6H_3Me_2\cdot CO\cdot CHBrMe$ [Me_2:CO = 1 : 4 : 2], is an oil distilling at 166—168° under 40—45 mm. pressure, and yields an *anilide* crystallising from alcohol in yellow needles and melting at 111°. The corresponding *ketone*, obtained from metaxylene, distils at 160—163° under a pressure of 20—25 mm.

Diphenyl α-bromethyl ketone, $C_6H_4Ph\cdot CO\cdot CHBrMe$, forms a white, crystalline powder, melts at 79—80°, is soluble in hot alcohol or in acetone, and when oxidised yields diphenylparacarboxylic acid.

Benzene reacts with phenyl-$\alpha\beta$-dibromopropionic chloride in the presence of aluminium chloride at the ordinary temperature, yielding *phenyl β-phenyl-αβ-dibromethyl ketone*, $Ph\cdot CO\cdot CHBr\cdot CHBrPh$, which crystallises in colourless needles melting at 88°. Claisen and Claparède have described a similar compound as melting at 156—157° (Abstr., 1882, 511). J. J. S.

The Cinnamic Acid Series. I. The Behaviour of Coumarin, the Coumaroles, and some other Derivatives to Metallic Sodium, and the accompanying Fluorescence Phenomena. By HERMANN KUNZ-KRAUSE (*Ber.*, 1898, 31, 1189—1193).—The author proposes to term ordinary coumarin *coumarole*, and to extend this nomenclature to its derivatives.

In the cinnamic acid series of compounds, only direct derivatives of coumarin yield sodium salts which form fluorescent aqueous solutions, the only exception being coumaric acid. Thus orthomethoxycoumaraldehyde, cinnamic acid itself, 3 : 4-dihydroxycinnamic acid, piperic acid, caffetannic acid, and piperine do not yield sodium salts of this character, whereas coumarin itself, umbelliferone, daphnetin, æsculetin, and β-methylæsculetin all form them. The author is of opinion that the fluorescence of these salts is not to be attributed to the presence of the coumarin group as such, but to the group formed from it by hydrolysis in alkaline solution, and this agrees with the fact that coumaric acid also yields a fluorescent sodium salt. β-Methylæsculetin forms two sodium compounds, $C_{10}H_8Na_2O_5$ and $C_{10}H_7Na_5O_5$, in both of which the lactone combination has been destroyed.

The solutions of derivatives of coumarin in aniline, pyridine, and quinoline are not fluorescent, and many of these compounds appear to form additive compounds with the bases named. A. H.

New Method of Preparing 1 : 3 : 4-Xylenesulphaminic Acid. By ALFRED JUNGHAHN (*Ber.*, 1898, 31, 1234—1236).—*Xylidine 1 : 3 : 4-xylenesulphaminate*, $C_6H_3Me_2\cdot NH\cdot SO_3H,C_6H_3Me_2\cdot NH_2$, is ob-

tained by passing dry sulphurous anhydride into unsymmetrical metaxylidine until the gas is no longer absorbed, and heating the crystals thus obtained at 170—180° during 5 hours in sealed tubes; the product is a mixture of xylidine, sulphur, and xylidine xylenesulphaminate, which crystallises from hot water in beautiful, colourless needles, and melts at 169—170°. The substance is also produced when chlorosulphonic acid is slowly added to a cold solution of 1 : 3 : 4-xylidine in chloroform; it is insoluble in benzene and petroleum, but dissolves readily in alcohol and in hot water, and is sparingly soluble in ether.

1 : 3 : 4-*Xylenesulphaminic acid*, $C_6H_3Me_2 \cdot NH \cdot SO_3H$, crystallises in pale red needles; it is obtained by treating a concentrated aqueous solution of the *ammonium* salt, which crystallises in white, lustrous leaflets, with half its volume of fuming hydrochloric acid. It dissolves readily in water, ethylic alcohol, and methylic alcohol, but is almost insoluble in benzene, petroleum, chloroform, and ether. The *barium* salt forms lustrous leaflets, and the *sodium* salt also crystallises in leaflets.

The acid described in this paper is the first aromatic sulphaminic acid which has been hitherto isolated. M. O. F.

Parabenzoyltoluene Derivatives. By PAUL BOURCET (*Bull. Soc. Chim.*, 1897, [iii], 17, 81—85. Compare Abstr., 1897, i, 566).—*Trinitroparabenzoyltriphenylmethane*, $NO_2 \cdot C_6H_3Bz \cdot CH(C_6H_4 \cdot NO_2)_2$, is obtained by slowly adding parabenzoyltriphenylmethane to a large excess of fuming nitric acid at 0°, finally warming gently on the water bath. As precipitated from this solution by water, it is a white powder, soon becoming yellow on exposure to light, but as obtained by evaporating the nitric acid solution, it forms yellowish, monoclinic crystals. It melts at 74—75°, is insoluble in water and light petroleum, slightly soluble in ether and alcohol, and very soluble in benzene, chloroform, and boiling acetic acid.

Trinitroparabenzoyltriphenylcarbinol, $NO_2 \cdot C_6H_3Bz \cdot C(C_6H_4 \cdot NO_2)_2 \cdot OH$, is prepared by oxidising the preceding compound with chromic acid in acetic acid solution, and, less easily, by direct nitration of parabenzoyltriphenylcarbinol. It is a colourless substance, becoming bright red on exposure to light, and crystallises with difficulty from ether, melts at about 88°, is insoluble in water and light petroleum, fairly soluble in alcohol and ether, very soluble in chloroform, benzene, and boiling acetic acid.

Parabenzoylpararosaniline acetate, $NH_2 \cdot C_6H_3Bz \cdot C(C_6H_4 \cdot NH_2)_2 \cdot OAc$, obtained by acting on an acetic acid solution of trinitroparabenzoyltriphenylcarbinol with the theoretical quantity of zinc powder, is a green, crystalline powder, the solution of which appears red by transmitted light. It is insoluble in benzene, soluble in alcohol and acetic acid, and dyes silk, wool, and cotton a fast green without a mordant.

Parabenzoylparaleucaniline, $NH_2 \cdot C_6H_3Bz \cdot CH(C_6H_4 \cdot NH_2)_2$, is prepared by reducing trinitroparabenzoyltriphenylcarbinol with excess of zinc and acetic acid; it forms colourless crystals, insoluble in water, somewhat soluble in alcohol, which decompose without melting when heated to 115°. N. L.

Transformations of Ethinediphthalide. I. By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, 31, 1159—1174).—The formula $C_6H_4<\substack{CO\\CO}>CH\cdot CH<\substack{CO\\CO}>C_6H_4$, ascribed by Nathanson (Abstr., 1894, i, 37) to bisdiketohydrindene, is identical with that given by Kaufmann to diphthalylethane. The authors have therefore investigated the reactions of bisdiketohydrindene and have found that they all agree with the formula of Nathanson. Bisdiketohydrindene readily yields a *potassium* salt, $C_{18}H_8K_2O_4$, which crystallises in brownish-red, quadratic plates, and is converted by methylic iodide into *dimethylbisdiketohydrindene*, $C_6H_4<\substack{CO\\CO}>CMe\cdot CMe<\substack{CO\\CO}>C_6H_4$, crystallising in colourless, rhombic tablets melting at 203—205°. The constitution of this compound is proved by the facts that it is not affected by boiling hydriodic acid, and that it is also formed by the oxidation of β-methyldiketohydrindene, $C_6H_4{:}(CO)_2{:}CHMe$. Bis-diketohydrindene is converted by oxidation with hydrogen peroxide in alkaline solution into *dihydroxybisdiketohydrindene*,

$$C_6H_4{:}(CO)_2{:}C(OH)\cdot C(OH){:}(CO)_2{:}C_6H_4,$$

which crystallises in yellow, pointed needles melting at 168—170° and is decomposed by boiling into phthalonic acid, $COOH\cdot C_6H_4\cdot CO\cdot COOH$, and anhydrobisdiketohydrindene, $C_6H_4<\substack{CO\\CO}>C{:}C<\substack{CH_2\\C_6H_4}>CO$, the latter being probably a secondary product, formed by the action of water on the diketohydrindene primarily produced. The hydroxy-compound is converted by acetic anhydride into *bisdiketohydrindene oxide*, $O<\substack{C{:}(CO)_2{:}C_6H_4\\ | \\ C{:}(CO)_2{:}C_6H_4}$, which crystallises in orange-yellow needles melting and decomposing at 216—218°. Hydriodic acid reduces the hydroxy-compound to isoethinediphthalide. Chlorine converts bisketodihydrindene into *dichlorobisdiketohydrindene*, $C_6H_4{:}(CO)_2{:}CCl\cdot CCl{:}(CO)_2{:}C_6H_4$, which crystallises in serrated crystals melting at about 298°. Aqueous potash converts it into the dihydroxy-compound described above, whilst hydriodic acid reduces it to bisdiketohydrin dene. It reacts with sodium methoxide to form a sodium salt,

$$COOMe\cdot C_6H_4\cdot CO\cdot CNa(OMe)\cdot C(OMe){:}(CO)_2{:}C_6H_4,$$

which crystallises in yellow tablets, and on acidification yields a substance which crystallises in faintly pink, rhombic tablets melting at 175—180°, and is probably *dimethoxybisdiketohydrindene*,

$$C_6H_4{:}(CO)_2{:}C(OMe)\cdot C(OMe){:}(CO)_2{:}C_6H_4.$$

Dibromobisdiketohydrindene, prepared in a similar manner to the dichloro-compound, is a white powder and decomposes above 250°.

Phosphorus pentachloride converts bisdiketohydrindene into the *monochloro*-derivative, $C_6H_4{:}(CO)_2{:}CCl\cdot CH{:}(CO)_2{:}C_6H_4$, which crystallises in serrated needles melting at 242—244°. Alcoholic sodium ethoxide converts this substance into *hydroxybisdiketohydrindene*,

$$C_6H_4{:}(CO)_2{:}C(OH)\cdot CH{:}(CO)_2{:}C_6H_4,$$

which crystallises in microscopic prisms melting at 171°, and is reduced by hydriodic acid to isoethinediphthalide and a second *compound*, $C_{18}H_{12}O_4$, which crystallises in colourless needles melting at 150°.

Sodium methoxide converts the monhydroxy-compound into a *sodium* salt, $OMe\cdot C_{18}H_8NaO_4 + \frac{1}{2}H_2O$, which on acidification yields *methoxybisdiketohydrindene*, $C_6H_4{:}(CO)_2{:}CH\cdot C(OMe){:}(CO)_2{:}C_6H_4$; this crystallises in flat prisms and melts and decomposes at about 230°. The crystalline *silver* salt is converted by methylic iodide into *methoxymethylbisdiketohydrindene*, $C_6H_4{:}(CO)_2{:}CMe\cdot C(OMe){:}(CO)_2{:}C_6H_4$, crystallising in colourless tablets melting at 214—216°. A. H.

Transformations of Ethinediphthalide. II. By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, **31**, 1272—1286).—*Isoethinediphthalide* (preceding abstract) is shown to be probably *dihydroxynaphthacenequinone*, $C_6H_4<\begin{matrix}C(OH)\cdot C\cdot CO\\ C(OH)\cdot C\cdot CO\end{matrix}>C_6H_4$, this formula being most in harmony with the reactions described below. It has been compared carefully with Kaufmann's indenigo (Abstr., 1897, i, 245), and the two substances appear to be identical, in which case the latter can no longer be regarded as diphthalylethylene.

Isoethinediphthalide is oxidised to phthalic acid by hydrogen peroxide in boiling alkaline solution. With potash, it forms a *potassium* salt, $C_{18}H_9KO_4$, dark bronze coloured and shot with green, but this is not acted on by potash, even at 300°; when heated with soda-lime at 390—400° in a bath of saltpetre, isoethinediphthalide is, however, partly resolved into phthalic and benzoic acids. Hydrochloric acid at 250° has no action on it.

When isoethinediphthalide is oxidised with fuming nitric acid at 100°, phthalic acid is formed. At the ordinary temperature, it yields a brown substance melting at 330—333°, which appears to be *naphthacenediquinone*, $C_6H_4<\begin{matrix}CO\cdot C\cdot CO\\ CO\cdot C\cdot CO\end{matrix}>C_6H_4$; it is reconverted into isoethinediphthalide by reduction with hydriodic acid and phosphorus, or by heating with potash at 300°, or boiling with 33 per cent. aqueous potash.

When distilled with zinc dust, isoethinediphthalide is reduced to *naphthacene*, $C_6H_4<\begin{matrix}CH\cdot C\cdot CH\\ CH\cdot C\cdot CH\end{matrix}>C_6H_4$, and *dihydronaphthacene*, $C_6H_4<\begin{matrix}CH\cdot C\cdot CH_2\\ CH\cdot C\cdot CH_2\end{matrix}>C_6H_4$; the latter of these is more soluble in benzene, and it is the product formed when isoethinediphthalide is reduced with hydriodic acid and phosphorus at 154—157°. Dihydronaphthacene melts at 206—207° and boils at about 400°; it is oxidised by chromic acid in boiling acetic acid solution to *naphthacenequinone*, $C_6H_4<\begin{matrix}CH\cdot C\cdot CO\\ CH\cdot C\cdot CO\end{matrix}>C_6H_4$, which is yellow, melts at 294°, and is converted by potash at 310°, into benzoic and 2-naphthoic acids and some isoethinediphthalide; by fuming nitric acid in acetic acid solution, into a yellow *mononitronaphthacenequinone* melting at 315°, and by distillation with zinc dust into naphthacene and dihydronaphthacene; with fuming nitric acid in acetic acid solution, dihydronaphthacene yields a *mononitronaphthacenequinone* melting at about 240°. Naphthacene

forms orange-yellow to reddish-yellow leafy crystals and melts near 335°, the exact temperature depending on the rate of heating; with fuming nitric acid in acetic acid solution it appears to yield naphthacenequinone; distilled with zinc dust it yields dihydronaphthacene.

Isoethinediphthalide forms orange-yellow *diacetyl* and *dibenzoyl* derivatives; these melt and decompose at 220—235° and 334—339° respectively. With a mixture of phosphorus oxychloride and pentachloride at 145°, it yields yellowish *dichloronaphthacenequinone*, $C_6H_4<\begin{matrix}CCl\cdot C\cdot CO\\ | \\ CCl\cdot C\cdot CO\end{matrix}>C_6H_4$; this melts at 259—260° (corr.), yields with aniline the brown *dianilidonaphthacenequinone* melting at 245°, and is reduced by hydriodic acid and phosphorus to dihydronaphthacene.

C. F. B.

Allofluorescein. By BRONISLAW PAWLEWSKI (*Ber.*, 1898, **31**, 1302).—A reply to R. Meyer (this vol., ii, 275).

The description of allofluorescein as a colourless, amorphous substance (Abstr., 1896, i, 50) is erroneous; under the microscope it is seen to be crystalline.

C. F. B.

Ethenyltriamidonaphthalene and its Acetyl Compound. By OSCAR MARKFELDT (*Ber.*, 1898, **31**, 1174—1178).—The primary azo-colouring matters derived from ethenyltriamidonaphthalene are only of small value, but the secondary disazo-compounds are not less valuable than the benzidine colouring matters, and dye unmordanted cotton, even in acid solution. Meldola and Streatfeild were unable to prepare an acetyl derivative of the base (Trans., 1887, 691), but this can readily be obtained by heating it with acetic anhydride and fused sodium acetate. The *acetate*, $CMe\lessgtr\begin{matrix}NH\\ N\end{matrix}>C_{10}H_5\cdot NHAc,C_2H_4O_2$, crystallises with 2 mols. of acetic acid in white, nacreous plates melting above 280°, whilst the *acetyl base* crystallises with $2H_2O$ in snow-white needles, with a satin lustre. The water is lost at 110°, and the anhydrous base then melts above 280°. *Acetylethenyltriamidonaphthalene hydrochloride* dissolves without decomposition in water, and crystallises in flat, white needles which become pink in the air. The *sulphate*, *nitrate*, and *picrate* have all been obtained well crystallised.

A. H.

Symmetrical Tetramethyldiamidodiphenyltetramethyldiamidodianthranol and the corresponding Oxanthranol. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1897, **125**, 286—288. Compare O. Fischer, Abstr., 1881, 587).—The condensation attempted by Fischer from tetramethyldiamidodiphenylmethaneorthocarboxylic acid is readily accomplished by using dimethylaniline and phosphorus oxychloride in place of sulphuric acid. The product, *symmetrical tetramethyldiamidodiphenyltetramethyldiamidodianthranol*,

$$NMe_2\cdot C_6H_3<\begin{matrix}C(C_6H_4\cdot NMe_2)\cdot C(C_6H_4\cdot NMe_2)\\ C_6H_4 \qquad\qquad C_6H_4\\ C(OH)\text{———}C(OH)\text{———}\end{matrix}>C_6H_3\cdot NMe_2,$$

crystallises from boiling toluene in yellow plates containing a molecule of toluene of crystallisation, which it loses when dried at 130°; it

melts at 275° and is readily oxidised, so much so that, on heating, it becomes phosphorescent. When an acid solution of this compound is oxidised with potassium dichromate, or with ferric chloride, an intense pure blue coloration is obtained; this is very fugitive, the colour slowly disappearing in the cold, and rapidly on heating. From concentrated solutions, colourless needles of *tetramethyldiamidophenyloxanthranol* are deposited; these dissolve readily in chloroform or nitrobenzene, but are only sparingly soluble in alcohol, ether, benzene, or toluene; they melt at 213° and dissolve in concentrated sulphuric acid, yielding a blue solution. The fugitive blue colour first formed is the chloride of the colourless carbinol, and its acid solution, on warming, is hydrolysed into the colourless oxanthranol and hydrochloric acid. The compound of the blue colouring matter with zinc chloride is more stable, and crystallises in small, bronzy needles, which, however, slowly turn colourless. J. J. S.

Terpenes and Ethereal Oils. Pulegenic Acid and Synthetical Pulegone. By OTTO WALLACH (*Annalen*, 1898, **300**, 259—277. Compare Abstr., 1896, i, 310).—*Methylic pulegenate* boils at 89—90° under a pressure of 10 mm.; it is prepared by the action of sodium methoxide dissolved in methylic alcohol on the hydrochloride. On acidifying the alkaline liquid which remains after methylic alcohol and the ethereal salt have been removed in a current of steam, the *lactone*, $C_{10}H_{16}O_2$, is precipitated; it boils at 125—127° under a pressure of 15 mm. The *acid*, $C_{10}H_{16}O_2$, produced along with it, boils at 145—147° and 256—260° under pressures of 15 mm. and 760 mm. respectively; it has the sp. gr. = 0·9955, and the refractive index $n_D = 1{\cdot}47547$ at 21°. Although closely resembling pulegenic acid, the substances are not identical, as the *amide* crystallises from very dilute methylic alcohol in needles, and melts at 152°.

Pulegenolide, $C_{10}H_{14}O_2$, produced by the action of alcoholic sodium methoxide on the brominated lactone obtained from pulegenic acid and potassium hypobromite, melts at 44—45°, and boils at 265—268° under atmospheric pressure. The *hydroxy-acid*, $C_{10}H_{16}O_3$, produced on hydrolysing the lactone with aqueous alkali, melts at 95°, and forms a *silver* salt. The hydroxylactone, $C_{10}H_{16}O_3$, obtained by oxidising pulegenic acid with potassium permanganate (*loc. cit.*), may be converted into pulegenolide by the action of phosphorus pentachloride and subsequent treatment of the product with alcoholic sodium methoxide; conversely, the brominated lactone obtained from pulegenic acid and potassium hypobromite yields the hydroxy-lactone under the influence of moist silver oxide. In view of these facts, the author ascribes to pulegenic acid the constitution $\begin{array}{l} CH_2\cdot CMe\cdot CH_2\cdot COOH \\ CH_2\cdot C\colon CMe_2 \end{array}$ representing the hydroxy-lactone and pulegenolide by the formulæ

$$\begin{array}{l} CH_2\cdot CMe—CH_2\cdot CO \\ CH_2\cdot C\cdot CMe(OH)\cdot O \end{array} \text{ and } \begin{array}{l} \quad CMe_2 — \\ CH_2\cdot C\cdot O\cdot CO—>CH \\ CH_2\cdot CMe—— \end{array} \text{ respectively.}$$

The remaining portion of the paper deals with compounds described in a preliminary communication (Abstr., 1897, i, 159). M. O. F.

Terpenes and Ethereal Oils. *Cis-* and *trans-***Isomerism in the Menthol Series.** By OTTO WALLACH [and D. F. WERNER] (*Annalen*, 1898, 300, 278—285. Compare Abstr., 1893, i, 724).—In view of the fact that dextrorotatory menthylamine yields a large proportion of menthene under the influence of nitrous acid, whilst *l*-menthol arises from the lævo-base, it follows that the menthol corresponding to dextrorotatory menthylamine loses water more readily than that derived from lævo-menthylamine. The latter is therefore referred to as *trans*-menthylamine, the dextrorotatory base being called *cis*-menthylamine.

trans-Menthylamine boils at 209—210°; it has sp. gr. = 0·86, and the refractive index $n_D = 1·46058$ at 20°. The *carbamide* melts at 134—136°, and the *phenylcarbamide*, crystallises from alcohol, and melts at 140—141°.

trans-*Menthylmethylnitrosamine*, $C_{10}H_{19}·NMe·NO$, is a yellow oil which boils at 145—146° under a pressure of 18—20 mm. trans-*Menthylethylnitrosamine*, $C_{10}H_{19}·NEt·NO$, crystallises from dilute methylic alcohol in colourless needles, melts at 52—53°, and boils at 155—156° under a pressure of 22 mm. trans-*Menthylpropylnitrosamine*, $C_{10}H_{19}·NPr^{\alpha}·NO$, boils at 159—161° under a pressure of 20 mm. trans-*Menthylisobutylnitrosamine*, $C_{10}H_{19}·N(C_4H_9)·NO$, forms white needles, melts at 52—53°, and boils at 160—161°.

trans-*Menthyltrimethylammonium iodide*, $C_{10}H_{19}·NMe_3I$, separates from water in large, colourless crystals, and melts at 190°; the *triiodide* melts at 117—118°. trans-*Menthyltrimethylammonium hydroxide*, $C_{10}H_{19}·NMe_3·OH$, is a colourless, crystalline, hygroscopic mass; distillation under atmospheric pressure resolves it into water, trimethylamine, and menthene.

cis-Menthylamine was previously obtained (*loc. cit.*) by heating *l*-menthone with ammonium formate, when a mixture of the lævo- and dextro-rotatory formylmenthylamines was produced, these being separated by fractional crystallisation. In attempting to utilise the acetyl derivative for this purpose, it was found that the compound must be heated with hydrochloric acid in a sealed tube at 140° before being completely hydrolysed.

cis-Menthylamine boils at 207—208°, has sp. gr. = 0·857, and the refractive index $n_D = 1·45940$. The *carbamide* and the *phenylcarbamide* melt at 155—156° and 177—178° respectively. cis-*Menthyltrimethylammonium iodide* crystallises from water, and melts at 160—161°; cis-*menthyltrimethylammonium hydroxide* is resolved into water, trimethylamine, and menthene on distillation. Menthene is also formed when an aqueous solution of *cis*-menthylamine hydrochloride is boiled with sodium nitrite. M. O. F.

Terpenes and Ethereal Oils. Pinocamphone, a New Camphor from Pinene. By OTTO WALLACH [and J. A. SMYTHE] (*Annalen*, 1898, 300, 286—293).—*Pinocarvone* is the name now given to the ketone, $C_{10}H_{14}O$, obtained by oxidising *pinocarveol*, $C_{10}H_{15}·OH$, derived from pinylamine (Wallach, Abstr., 1894, i, 45); the *semicarbazone* of pinocarvone crystallises from dilute methylic alcohol, and melts at 204°.

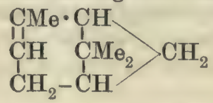
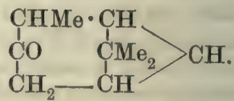
Pinocamphone, $C_{10}H_{16}O$, is a bye-product in the preparation of pinylamine from nitrosopinene, zinc dust, and glacial acetic acid, and represents 20 per cent. of the material employed; it has the odour of turpentine, and suggests peppermint oil when heated. The ketone boils at 211—213° under atmospheric pressure; it has the sp. gr. $=0{\cdot}959$, and the refractive index $n_D=1{\cdot}47273$ at 21°. The *semicarbazone* melts at 199—200°, and the *oxime* is volatile in an atmosphere of steam, crystallises in large, transparent plates, and melts at 86—87°.

Pinocampheol, $C_{10}H_{17}{\cdot}OH$, is obtained by reducing pinocamphone with sodium in aqueous ether, and forms a viscous liquid having the odour of terpineol and turpentine; it boils at 218—219°, has the sp. gr. $=0{\cdot}9655$, and the refractive index $n_D=1{\cdot}48612$ at 20°. The *phenylurethane* melts at 98°.

Pinocamphonitrile, $C_{10}H_{15}N$, is the product of treating pinocamphone-oxime with boiling sulphuric acid (1 : 1); a portion of the oxime remains unchanged.

Reduction of nitrosopinene bromide has yielded a *ketone*, $C_{10}H_{16}O$, isomeric with pinocamphone, and having the odour of carvone; it closely resembles the inactive dihydrocarvone, and the *oxime* melts at 113—114°. A *base* is formed along with it which boils at 217—220°, and has the sp. gr. $=0{\cdot}918$.

Representing pinene by the formula I., the author regards pinocamphone as having the constitution II.

I.  II. 

M. O. F.

Terpenes and Ethereal Oils. Fénchone. By OTTO WALLACH (*Annalen*, 1898, **300**, 294—322. Compare Abstr., 1895, i, 380).—The difficulties hitherto attending the production of purified fenchocarboxylic acid have now been removed. There are found to be two isomeric acids of this description, distinguished by the author as α- and β-fenchocarboxylic acids. In order to separate these two substances, the crude product of the action of carbonic anhydride on an ethereal solution of fenchone in presence of sodium is submitted to distillation under a pressure of 15 mm., the fraction which boils at 150—180° solidifies in the receiver, and consists of the isomeric fenchocarboxylic acids along with small quantities of hydroxycarbofenchonone (see below), and the anhydro-acid, $C_{11}H_{16}O_2$. The mixture is therefore treated with ammonia or caustic soda, agitated with ether, and the aqueous liquor acidified; α-fenchocarboxylic acid crystallises from the product more rapidly than the β-derivative, which is also more readily soluble in light petroleum than the isomeride; this is therefore washed with this agent, and finally crystallised from dilute acetic acid.

α-Fenchocarboxylic acid, $OH{\cdot}C_{10}H_{16}{\cdot}COOH$, crystallises from acetic acid in transparent prisms, and melts at 141—142°, although this

constant is very materially depressed by contamination with the β-acid; it boils at 175° under a pressure of 11 mm., and does not undergo decomposition. The *lead* salt is readily soluble in ether, which also dissolves the *silver* salt; the latter is almost insoluble in water, but dissolves in chloroform and in methylic iodide. α-Fenchocarboxylic acid is optically active, a 4·5 per cent. ethereal solution having the specific rotatory power $[\alpha]_D = +11·28°$. On mixing equal weights of the acid obtained from *d*-fenchone and from *l*-fenchone, an inactive *racemic acid* is produced, which melts at 91—92°.

Anhydrofenchocarboxylic acid, $C_{11}H_{16}O_2$, is formed on distilling α-fenchocarboxylic acid under atmospheric pressure, water being eliminated; it dissolves with great difficulty in water, and is volatile in an atmosphere of steam, differing in this respect from α-fenchocarboxylic acid. The substance boils at 275—277° under atmospheric pressure, and, after crystallisation from dilute acetone, melts at 175°; the *lead* salt is insoluble in ether. The anhydro-acid is also formed when α-fenchocarboxylic acid is fused with potash.

Hydroxycarbofenchonone, $C_{11}H_{16}O_2$, the yellow ketone obtained on distilling lead α-fenchocarboxylate in a vacuum, crystallises from petroleum in yellow, transparent plates or prisms, having the appearance of a uranium salt, has a feeble, camphor-like odour, melts at 96°, and boils at 273—274° under atmospheric pressure. The *oxime* crystallises from methylic alcohol in colourless, transparent needles, and melts at 108°; reduction with sodium in alcoholic solution converts it into a *base* which melts at 74°, and is not volatile in an atmosphere of steam. The *compound*, $C_{11}H_{17}NO$, is obtained by the action of ammonia on the ketone, which loses its yellow colour; the substance separates from alcohol in colourless crystals, and melts at 205°. The yellow ketone dissolves in warm caustic soda, undergoing conversion into β-fenchocarboxylic acid; it is probably a cyclic orthohydroxyketone.

β-Fenchocarboxylic acid is prepared by digesting hydroxycarbofenchonone with excess of warm, dilute caustic soda on the water bath until dissolution is complete, and the liquid is almost colourless; it separates in opaque, indefinite crystals on diluting the acetic acid solution, and melts at 76—77°. The acid is dextrorotatory, but is less active than the isomeride; it is also less stable, yields fenchylic alcohol and anhydrofenchocarboxylic acid when heated under atmospheric pressure, and is in part converted into the α-acid in a vacuum. Sodium hypobromite or an acid solution of potassium permanganate give rise to fenchone. The *lead* and *silver* salts do not differ very materially from those of the isomeric acid. The α- and β-fenchocarboxylic acids may be regarded as the *trans*- and *cis*-modifications respectively.

The *lactone*, $C_{10}H_{16}O_2$, is obtained by oxidising α-fenchocarboxylic acid with an amount of potassium permanganate corresponding with three atomic proportions of oxygen; it crystallises from dilute methylic alcohol, and melts at 64·5°, boiling at 150° under a pressure of 14 mm.

Representing fenchone by the formula $C_7H_{12}{<}\begin{matrix}CHMe\\|\\CO\end{matrix}$, the fencho-

carboxylic acids have the constitution $C_7H_{14}<\begin{smallmatrix}CHMe\\ |\\ C(OH)\cdot COOH\end{smallmatrix}$; anhydrofenchocarboxylic acid, hydroxycarbofenchonone, and the lactone, $C_{10}H_{16}O_2$, which are isomeric, are then expressed by the formulæ

$$C_7H_{12}<\begin{smallmatrix}CMe\\ ||\\ C\cdot COOH\end{smallmatrix},\quad C_7H_{12}<\begin{smallmatrix}CMe-\\ |\\ C(OH)\end{smallmatrix}>CO \text{ and } C_7H_{12}<\begin{smallmatrix}CHMe\\ CO-\!-\end{smallmatrix}>O$$

respectively.

Methylic fencholenate *hydrochloride*, $C_9H_{16}Cl\cdot COOMe$, is obtained by saturating a solution of fencholenic acid in methylic alcohol with hydrogen chloride; it boils at 124—125° under a pressure of 14 mm. *Methylic* fencholenate, $C_9H_{15}\cdot COOMe$, is produced when the hydrochloride is treated with sodium methoxide; it boils at 97—98° under a pressure of 13 mm., and has an agreeable, geranium-like odour.

Fencholenic alcohol, obtained by reducing the amide with sodium in ethylic alcohol (Abstr., 1895, i, 381), is not identical with the compound obtained by the action of nitrous acid on fencholenamine (Abstr., 1892, 1240). The latter boils at 94—96° under a pressure of 20 mm., has sp. gr. = 0·922, and the refractive index $n_D = 1·4732$; it does not yield fenchenole when treated with hot dilute sulphuric acid.

Fenchelene, $C_{10}H_{16}$, is a bye-product in the formation of fencholenic alcohol, and boils at 66—70° and 175—178° under pressures of 20 mm. and 760 mm. respectively; it has sp. gr. = 0·842, and the refractive index $n_D = 1·47439$ at 20°.

The *lactone*, $C_{10}H_{15}BrO_2$, is obtained by the action of potassium hypobromite on a solution of potassium fencholenate; it crystallises from light petroleum, and melts at 56°.

Hydroxyfenchenic acid, $OH\cdot C_9H_{14}\cdot COOH$, is the chief product of oxidising fenchene with potassium permanganate; it melts at 152—153° (compare Abstr., 1891, 1086).

Fenchocamphorone, $C_9H_{14}O$, is obtained by the oxidation of hydroxyfenchenic acid with sodium hypochlorite, chromic acid, potassium permanganate, or lead peroxide with sulphuric acid; it melts at 109—110°, and boils at 202°. The ketone is isomeric with phorone, and has the odour of camphor, from which it is distinguishable with difficulty. The *oxime* melts at 69—71°, and yields a nitrile on treatment with dilute sulphuric acid.

Fenchocamphorol, $C_9H_{15}\cdot OH$, results on reducing fenchocamphorone with sodium in aqueous ether; it crystallises from dilute methylic alcohol in needles, and melts at 128—130°.

Fenchocamphorone is oxidised by dilute nitric acid (sp. gr. = 1·25), yielding two acids which crystallise from water, and melt at 124° and 202° respectively; the latter *compound* probably has the composition $C_9H_{14}O_4$, and yields a *silver* salt which shows it to be dibasic.

The author considers that the formula $CH\begin{smallmatrix}\diagup CHMe\cdot CO\diagdown\\ -\!-CMe_2-\!-\\ \diagdown CH_2-CH_2\diagup\end{smallmatrix}CH$ represents the structure of fenchone more accurately than the expression

already suggested (Abstr., 1895, i, 382). If this is accepted, fenchene, hydroxyfenchenic acid, and fenchocamphorone will be represented by the formulæ $CH\left\langle\begin{matrix}CMe{:}CH\\ CMe_2\\ CH_2\cdot CH_2\end{matrix}\right\rangle CH$, $CH\left\langle\begin{matrix}C(OH)(COOH)\cdot CH_2\\ CMe_2\\ CH_2 \text{———} CH_2\end{matrix}\right\rangle CH$ and $CH\left\langle\begin{matrix}CO\text{—}CH_2\\ CMe_2\\ CH_2\cdot CH_2\end{matrix}\right\rangle CH_2$ respectively.

M. O. F.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1898, 300, 322—357. Compare this volume, i, 89).—Usnic acid is found in *Cladina silvatica* (L.), *Cl. alpestris* (Rabenh.), and in *Cladonia amaurocraea* (Flörke); contrary to the statement of Rochleder and Heldt, genuine *Cladonia rangiferina* (L.) contains no trace of this acid.

Gyrophoric acid, hitherto only recognised by Stenhouse in *Umbilicaria pustulata* (L.) and *Ochrolechia tartarea* (L.), has now been found in *Gyrophora hirsuta* (Ach.) and *G. deusta* (L.).

Umbilicaric acid occurs in *Gyrophora polyphylla* (L.), *G. hyperborea* (Hoffm.), and in *G. deusta* (L.).

Cetraria fahlunensis (Ach.), *Cladina rangiferina* (L.), and *Cl. silvatica* (L.) contain cetraric acid, previously found in *Cetraria islandica* (L.).

The author has already enumerated forty-one lichens which contain atranoric acid; to these must be added *Sphyridium placophyllum* (Nahlbg.), *Cladina rangiferina* (L.), *Parmelia acetabulum* (Neck.), and *Cetraria fahlunensis* (Ach.).

Salazinic acid has been found in *Stereocaulon salazinum* (Bory), *Alectoria cana* (Ach.), *Parmelia perforata* (Ach.), *P. excrescens* (Arnold), *P. conspersa* (Ehrh.), and *Everniopsis Trulla* (Ach.); it has been also recognised in *Parmelia acetabulum.*

Hæmatomma ventosum (L.) contains divaricatic acid. *Divaricatinic acid* is produced along with orcinol, when this substance is heated with dilute caustic potash; it crystallises from benzene in microscopic, lustrous prisms, and melts at 149°, evolving gas.

Hesse's coccellic acid, occurring in *Cladonia coccifera,* has been found by the author in *Cl. amaurocraea* (Flörke).

Sphærophorin, which melts at 138—139°, and *sphærophoric acid* have been isolated from *Sphærophorus fragilis* (L.) and *Sph. coralloïdes* (Pers.); the first-named lichen contains also *fragilin,* a golden-yellow substance resembling lichen-chrysophanic, acid and other derivatives of anthracene in its colour reactions.

Physodalic acid and *physodalin* have been obtained from *Parmelia physodes* and *Parmelia pertusa* (Schrk.).

Mannitol has been found in *Callopisma vitellinum* (Ehrh.).

M. O. F.

Action of Benzylideneaniline on the Ethereal Salts of Unsaturated α-Hydroxy-acids. By ROBERT SCHIFF and L. GIGLI (*Ber.*, 1898, 31, 1306—1310).—In a preceding abstract (this vol., i, 464), reasons are given for supposing that the ethereal salts of so-called α-ketonic acids

really exist in the α-hydroxy (enolic) form, CHR:C(OH)·COOEt. These salts are known, in the case of ethylic oxaloacetate, [R = COOEt], to form compounds with benzylideneaniline, CHPh:NR' [R' = Ph], (Abstr., 1897, i, 293); such compounds must be regarded as α-hydroxypyrrolones, $\begin{matrix}\mathrm{CR\cdot CHPh} \\ \mathrm{C(OH)\cdot CO}\end{matrix}\!\!>\!\mathrm{NR'}$, in this particular case, as the enolic form of ethylic diphenyldihydrodiketopyrrolinecarboxylate. Similar enolic forms, enumerated below with their decomposing points, have been prepared by fusing benzylideneaniline (or β-naphthylamine) with various ethylic salts; all of them, in benzene solution, give a blood-red coloration with ferric chloride; when warmed with excess of free hydroxylamine, they are converted, according to the authors, into the ketonic forms, which then yield monoximes.

3-*Acetyl*-1 : 2-*diphenyldiketodihydropyrroline*, [R = Ac; R' = Ph], 239—240°; *oxime*, 213—215°. 3-*Benzoyl*-1 : 3-*diphenyldiketodihydropyrroline*, [R = Bz; R' = Ph], 250—252°; *oxime*, 213—215°. 3-*Benzoyl-2-phenyl*-1-β-*naphthyldiketodihydropyrroline*, [R = Bz; R' = $C_{10}H_{17}(\beta)$], 252—254°. 3-*Cinnamoyl*-1 : 2-*diphenyldiketodihydropyrroline*, [R = CO·CH:CHPh; R' = Ph], 230—231°; this substance was prepared from *ethylic benzylideneacetoneoxalate*, CHPh:CH·CO·CH:C(OH)·COOEt, which was itself obtained by condensing benzylideneacetone with ethylic oxalate, in cooled alcoholic solution, by means of sodium ethoxide, is yellow, melts at 84°, gives a coloration with ferric chloride, and condenses with phenylhydrazine, when warmed with it in acetic acid solution, to a compound, $\mathrm{CHPh{:}CH\cdot C}\!<\!\begin{matrix}\mathrm{N—NPh} \\ \mathrm{CH{:}C\cdot COOEt}\end{matrix}$, melting at 120°.

With pyruvic acid, a substance which exists in the ketonic form and gives no coloration with ferric chloride, benzylideneaniline does not condense readily; the product is an unstable, half-solid substance, decomposing at 147—148°, and giving no coloration with ferric chloride; presumably it is the ketonic form of *diphenyldiketodihydropyrroline*, $\begin{matrix}\mathrm{CH_2\cdot CHPh} \\ \mathrm{CO\text{———}CO}\end{matrix}\!\!>\!\mathrm{NPh}$.

C. F. B.

Pyridine Derivatives of Ethylic Cyanacetate. By Giorgio Errera (*Ber.*, 1898, 31, 1241—1246. Compare this vol., i, 297).—Ethylic 2 : 6-dihydroxydinicotinate, [2 : 6-dihydroxypyridine-3 : 4-dicarboxylate], $\mathrm{CH}\!<\!\begin{matrix}\mathrm{C(COOEt){:}C(OH)} \\ \mathrm{C(COOEt)\cdot C(OH)}\end{matrix}\!\!>\!\mathrm{N}$, produced when the diamide of ethylic dicarboxyglutaconate (this vol., i, 289) is dissolved in concentrated sulphuric acid, crystallises from water, alcohol, and benzene, and melts at 199° (compare Guthzeit, Abstr., 1894, i, 71). The salt is also formed by the action of caustic soda on ethylic cyanocarboxyglutaconate, $C(COOEt)_2$:CH·CNa(CN)·COOEt, the condensation product of ethylic ethoxymethylenemalonate with ethylic cyanacetate; the *sodium* derivative contains $2H_2O$, which is lost at 130°. When the salt or the diamide of ethylic dicarboxyglutaconate is boiled with dilute caustic soda (2 mols.), the *sodium* salt of monethylic 2 : 6-di-

hydroxydinicotinate, $CH\lessgtr\begin{matrix}C(COOH):C(OH)\\C(COOEt)\cdot C(OH)\end{matrix}\gtrless N$, is produced; it dissolves readily in hot alcohol and water, crystallising in colourless, microscopic needles containing $2H_2O$.

Ethylic 2 : 6-dihydroxypyridine-3-carboxylate,

$$CH\lessgtr\begin{matrix}C(COOEt):C(OH)\\CH\text{———}C(OH)\end{matrix}\gtrless N,$$

is obtained by eliminating carbonic anhydride from the foregoing substance, and crystallises from alcohol in colourless needles melting at 179°, when it becomes red and evolves gas; the *sodium* salt is crystalline.

Ethylic bromo-2 : 6-dihydroxypyridine-3-carboxylate,

$$C_5H_3BrNO_2\cdot COOEt,$$

is prepared by the action of bromine water on an aqueous solution of ethylic dihydroxypyridinecarboxylate; it crystallises from alcohol in white needles, and becomes black at 200°.

2 : 6-Dihydroxypyridine, $CH\lessgtr\begin{matrix}CH:C(OH)\\CH\cdot C(OH)\end{matrix}\gtrless N$, obtained from ethylic dihydroxypyridinecarboxylate and excess (3 mols.) of caustic soda, crystallises from water, and melts at 195°. It is identical with the compound obtained by Ruhemann, on boiling ethylic dihydroxydinicotinate with concentrated hydrochloric acid. The *hydrochloride* forms colourless, transparent needles, and melts, evolving gas, at 193°.

M. O. F.

New Synthesis of 2′-Amidoquinoline. By ROBERT PSCHORR (*Ber.*, 1898, **31**, 1289—1298).—*a-Paranitrophenylorthacetamidocinnamonitrile*, $NHAc\cdot C_6H_4\cdot CH:C(CN)\cdot C_6H_4\cdot NO_2$, obtained by adding 10 per cent. alcoholic sodium ethoxide to a solution of orthacetamidobenzaldehyde and paranitrobenzylic cyanide in alcohol at 50—45°, is yellow, and melts at 214—215° (corr.). When it is mixed, in alcoholic solution, at the ordinary temperature, with some caustic soda, it is converted into *2′-acetamido-3′-paranitrophenylquinoline*,

$$C_6H_4<\begin{matrix}CH:C\cdot C_6H_4\cdot NO_2\\N=C\cdot NHAc\end{matrix},$$

which melts at 219—220° (corr.). If the reaction is carried out at 100°, the product is *2′-amido-3′-paranitrophenylquinoline*, which can also be obtained from the acetamido-compound by the action of hydrochloric acid at 100°; this is yellow and melts at 258° (corr.); its picrate decomposes at about 270°; in acetic acid solution, it is converted by sodium nitrite into yellowish *3′-paranitrophenyl-2′-carbostyril*, $C_6H_4<\begin{matrix}CH:C\cdot C_6H_4\cdot NO_2\\N=C\cdot OH\end{matrix}$, which melts at 326° (corr.). The yield in these reactions is about 60 per cent. of the theoretical. 2′-Amido-3′-phenylquinoline and 2′-amidoquinoline itself can be prepared in the same way; the transformation is best effected by sodium ethoxide in alcoholic solution and with the aid of heat; under these circumstances, the acetyl group is eliminated at the same time, and no acetamidoquinoline is obtained.

2′-Amido-3′-phenylquinoline is obtained by boiling an alcoholic solu-

tion of 2-acetamidobenzaldehyde and benzylic cyanide with sodium ethoxide for a short time, and diluting the cooled product with water; it melts at 155—156° (corr.), and boils above 360°, almost without decomposing; its *picrate* melts at 234°. It yields 3′-*phenyl-2′-carbostyril*, identical with the substance obtained from 2-amidobenzaldehyde and sodium phenylacetate at 130°; this melts at 235° (corr.).

Orthamidocinnamonitrile is yellowish and melts at 134—135° (corr.); its *picrate* melts at 192—193° (corr.), its *acetyl* derivative at 172—174° (corr.). 2′-Amidoquinoline melts at 129° (not 114°, Ephraim, Abstr., 1891, 1510); the *picrate* decomposes at 250—253° (corr.). The nitrile could not be obtained from 2-amidobenzaldehyde and acetonitrile; it was prepared from orthonitrocinnamic acid by treating this with phosphorus oxychloride and pentachloride, converting the chloride, in benzene solution by a current of gaseous ammonia, into the *orthonitrocinnamic amide*, which melts at 185° (corr.); and boiling this with thionyl chloride in toluene solution, or, better, distilling it with phosphoric anhydride, when *orthonitrocinnamonitrile*, melting at 92° (corr.) and boiling at 194—196° under 7—8 mm. pressure, is obtained, and can be reduced to the amido-compound in alcoholic solution by tin and hydrochloric acid. C. F. B.

Ketones of the Tropine Group. IX. The Tropylamines. By Richard Willstätter and Wilhelm Müller (*Ber.*, 1898, **31**, 1202—1214. Compare this vol., i, 159).—Tropinonoxime can be converted by different methods of reduction into two different isomeric tropylamines. *ψ-Tropylamine*, $C_8NH_{14}\cdot NH_2$, is produced when the oxime is reduced by metallic sodium and boiling amylic alcohol, and is an oil which boils at 213° (corr.), and has a slight smell of piperidine; it readily unites with atmospheric carbonic anhydride, forms a cloud with hydrogen chloride, and is miscible with ether, alcohol, and water. It is a strong diacid base and precipitates hydroxides from the solutions of many metallic salts. The *hydrochloride, hydrobromide*, and *hydriodide* are readily soluble in water; the *aurochloride* melts and decomposes at 223—224°, and the *platinochloride* crystallises with $2H_2O$ in rhombohedral plates, which become anhydrous at 105°, and melt and decompose at 257°. The *carbamate* can be sublimed in long needles, whilst the *dithiocarbamate*, $C_8NH_{15}<\begin{matrix}NH\\S\end{matrix}>CS$, crystallises in lustrous plates which melt and decompose at 204—205°. *ψ-Tropylphenylthiocarbamide*, $C_8NH_{14}\cdot NH\cdot CS\cdot NHPh$, crystallises in lustrous prisms melting at 172°. ψ-Tropylamine is unaltered by prolonged boiling with a concentrated solution of sodium amyloxide.

Tropylamine is produced when tropinonoxime is reduced by sodium amalgam in acetic acid solution, and closely resembles the ψ-compound. It is an oil which boils at 211° (corr.) and forms readily soluble salts with the halogen acids. The *picrate* crystallises in characteristic plates which melt and decompose at 235°. The *platinochloride* is much less soluble than that of the ψ-base, and yields anhydrous crystals melting and decomposing at 257°. The *dithiocarbamate* crystallises in characteristic aggregates of small plates and melts at 194—195°.

Tropylphenylthiocarbamide crystallises in tablets, prisms, and needles, and melts at 142—143°. When tropylamine is boiled with a concentrated solution of sodium amyloxide in amylic alcohol, it is to a great extent converted into ψ-tropylamine, a small residue of the original base being, however, always left.

The authors propose the following formulæ for these two compounds, which they regard as geometrically isomeric.

$$\begin{array}{lll} CH_2—CH & \text{———} & CH_2 \\ | \quad\; CH_2 & NH_2\cdot CH & \\ NMe\cdot CH & \text{———} & CH_2 \end{array} \qquad \begin{array}{lll} CH_2—CH—CH_2 \\ | \quad\; CH_2 \;\; CH\cdot NH_2. \\ NMe\cdot CH—CH_2 \end{array}$$

A. H.

Indigo-oxime. By JOHANNES THIELE and ROBERT H. PICKARD (*Ber.*, 1898, **31**, 1252—1253).—Finely divided indigo is warmed with caustic soda on the water bath, and in a vessel from which the air has been driven out by hydrogen, and agitated with 2 parts of hydroxylamine hydrochloride; on filtering the liquid into cold, dilute hydrochloric acid, *indigo-oxime*, $C_{16}H_{11}N_3O_2$, separates as a brownish-violet, voluminous precipitate; it is washed with boiling water, and recrystallised from alcohol, separating in small, brownish-violet needles, having metallic reflex; it melts and decomposes at 205°. Hot hydrochloric acid does not liberate indigo from the substance; dilute caustic soda dissolves it, the deep red solution rapidly becoming brown when exposed to air. The solution in concentrated sulphuric acid is green, becoming blue when heated, a blue precipitate separating on dilution with water.

A blue substance is also precipitated when zinc dust is added to the alkaline solution, and quickly redissolves; the coloured liquid thus produced deposits a blue, amorphous precipitate on exposure to air. The compound, which is probably indigo-imide,

$$C_6H_4<^{CO}_{NH}>C:C<^{C(:NH)}_{—NH—}>C_6H_4,$$

froms a green solution in concentrated sulphuric acid, becoming blue when heated; alkaline hydroxylamine regenerates indigo-oxime.

Pentacetyloxyamidodiindyl, $C_6H_4<^{C(OAc)}_{-NAc-}>C\cdot C<^{C(NAc_2)}_{—NAc—}>C_6H_4$, is obtained by heating indigo-oxime with zinc dust, anhydrous sodium acetate, and acetic anhydride; it separates from alcohol as a straw-coloured, crystalline powder, and melts at 176°, decomposing at 180°. Hot caustic soda yields a solution of indigo white.

M. O. F.

Compounds of Antipyrine with Aldehydes. By GUSTAVE PATEIN (*Compt. rend.*, 1897, **125**, 956—959. Compare Knorr, Abstr., 1884, 1378; 1887, 601; and Schuftan, Abstr., 1895, i, 482).—Knorr's compounds of antipyrine with aldehydes are most readily obtained by the following method. The aldehyde (1 mol.), antipyrine (2 mols.), and water are mixed together, and hydrochloric acid is added until solution is complete; after several hours, the crystalline mass which has formed is rendered alkaline with ammonia, the crystals separated, and re-

crystallised from dilute alcohol. The compounds thus obtained are true methane derivatives of the type $(C_{11}H_{11}N_2O)_2CH_2$ or

$$(C_{11}H_{11}N_2O)_2CHR.$$

Simple aldehydes do not yield derivatives in which the carbon of the aldehyde becomes united to the nitrogen of antipyrine. Chloral, on the other hand, yields no methane derivative, but a compound composed of one molecule of chloral with one of antipyrine.

J. J. S.

Constitution of the Safranines. V. By George F. Jaubert (*Ber.*, 1898, 31, 1178—1189. Compare Abstr., 1895, i, 527).—When a mixture of equal molecules of paraphenylenediamine and methylmetaphenylenediamine is oxidised with potassium dichromate, a methylamidoeurhodine, $NH_2\cdot C_6H_3{<}{N \atop N}{>}C_6H_3\cdot NHMe$, is produced. If, however, methylmetatolylenediamine be employed, the product consists of *methyltolusafranine*, $NH_2\cdot C_6H_3{<}{N \atop NMe}{>}C_6H_2Me{:}NH$, which possesses all the properties of the safranines, forms a red solution in water, and dyes cotton on tannin in shades which are fast towards alkalis.

Ethyltolusafranine, $NH_2\cdot C_6H_3{<}{N \atop NEt}{>}C_6H_2Me{:}NH$, is prepared in a similar manner from ethylmetatolylenediamine [$Me : NH_2 : NHEt = 1 : 2 : 4$], and forms a green, crystalline *hydrochloride*. It readily yields a violet-blue diazo-compound, which reacts with β-naphthol to form a blue colouring matter. When it is diazotised in alcoholic solution, it yields *ethyltoluaposafranine*, $C_6H_4{<}{N \atop NEt}{>}C_6H_2Me{:}NH$, which is a microcrystalline powder with a bright green lustre. It forms a carmine-red solution in water, whilst the solution in hydrochloric acid is bluish-violet, and that in sulphuric acid green.

Trinitrometamidodiphenylamine [*trinitrophenylmetaphenylenediamine*], $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_3$, is prepared by the action of picrylic chloride on metaphenylenediamine, and forms orange-red crystals, melting at 206—207°, which are readily soluble in alkalis. It can readily be converted into a diazo-compound, which yields an orange colouring matter with salicylic acid. When oxidised in presence of paraphenylenediamine hydrochloride, it yields *trinitrophenylsafranine*, $N{<}{C_6H_3({:}NH) \atop C_6H_3(NH_2)}{>}N\cdot C_6H_2(NO_2)_3$, which produces very blue shades on cotton. The formation of a safranine in this way disproves the theory formulated by Nietzki (Abstr., 1895, i, 624) to explain this reaction, since all the ortho-positions in one benzene ring are occupied. *Trinitrophenylaposafranine*, $N{<}{C_6H_3({:}NH) \atop C_6H_4}{>}N\cdot C_6H_2(NO_2)_3$, prepared in the usual manner, closely resembles ordinary aposafranine, but is precipitated by weaker alkalis. *Trinitrophenyldimethylmetaphenylenediamine* forms reddish-brown crystals, and when oxidised in the presence of paraphenylenediamine hydrochloride yields *trinitrodimethylphenosafranine*,

which crystallises in needles with a green lustre and closely resembles the non-methylated compound, yielding a blue-colouring matter when β-naphthol is added to its diazo-solution, and being converted into the corresponding *aposafranine* when diazotised in alcoholic solution.

Methylphenotolylaposafranine, $N\lessgtr^{C_6H_2Me(:NH)}_{C_6H_4}>N\cdot C_6H_4Me$, is formed by the replacement of the amido-group of the safranine T of commerce by hydrogen, and forms a green, crystalline *hydrochloride*.

Ethylsafranol, $N\lessgtr^{C_6H_3O}_{C_6H_3(OH)}>NEt$, can readily be obtained by the action of paranitrosophenol on ethylmetamidophenol in alkaline solution, and is a brown, crystalline powder, with a bright green surface lustre. The *sodium* salt, $C_{14}H_{11}N_2O_2Na$, crystallises readily, and is insoluble in concentrated alkalis.

Phenylsafranolcarboxylic acid, $O:C_6H_4\lessgtr^{N}_{NPh}>C_6H_2(OH)\cdot COOH$, is prepared by oxidising a mixture of metahydroxydiphenylamine and paramidosalicylic acid. The *sodium* salt is a red, crystalline powder, which is freely soluble in water, whilst the free acid is a red, flocculent precipitate. *Phenylsafranolsulphonic acid*,

$$N\lessgtr^{C_6H_3O}_{C_6H_3(OH)}>N\cdot C_6H_4\cdot SO_3H,$$

formed by the action of metahydroxydiphenylaminesulphonic acid on paranitrosophenol, is a brown, crystalline powder with a green surface lustre. The *sodium* salt is readily soluble in water. *a-Naphthylsafranol* and the corresponding β-derivative are green, crystalline powders, and correspond in properties with the other members of the class.

Ethylsafraninone, $O:C_6H_3\lessgtr^{N}_{NEt}>C_6H_3\cdot NH_2$, is formed by the action of ethylmetamidophenol on nitrosoaniline, and forms a red, crystalline *hydrochloride*, which dissolves in sulphuric acid to form a dirty-green coloured solution showing the characteristic dichroism of the rosindone derivatives.

Ethyltoluaposafranone, $C_6H_4\lessgtr^{N}_{NEt}>C_6H_2MeO$, formed when ethyltoluaposafranine is boiled with 75 per cent. sulphuric acid, crystallises in small, brown needles, which yield a dichroitic solution in sulphuric acid. A. H.

Formation of Imido-1 : 2-diazole [1 : 2 : 3-Triazole] Derivatives from Aromatic Azimides and Ethereal Salts of Acetylenecarboxylic Acids. By ARTHUR MICHAEL, F. LUEHN, and HOWARD H. HIGBEE (*Amer. Chem. J.*, 1898, **20**, 377—395).—*Methylic* n-*phenyl-1 : 2-imidodiazoledicarboxylate* [*methylic* 1-*phenyl*-1 : 2 : 3-*triazole*-4 : 5-*dicarboxylate*], $N\lessgtr^{NPh\cdot C\cdot COOMe}_{N\text{---}C\cdot COOMe}$, obtained by heating together equivalent amounts of phenylazimide and methylic acetylenedicarboxylate for 5 hours at 100°, crystallises from alcohol in white needles melting

at 127—128°. On hydrolysis, it yields the *free acid*, isomeric but not identical with Pechmann's *n*-phenylosotriazolecarboxylic acid (*Annalen*, 262, 311). It crystallises from water in long, prismatic needles melting and decomposing at 149—150°. The *silver* salt forms white needles sparingly soluble in cold water, and the *calcium* salt white, truncated prisms grouped together in star-like forms.

When the free acid is heated for some time at 150°, carbonic anhydride is given off from both carboxyl groups and n-*phenyl*-1:2-*imidodiazole* [1-*phenyl*-1:2:3-*triazole*], $\begin{matrix} N{=\!=}N \\ | \\ CH{:}CH \end{matrix}\!>\!NPh$, is formed as white crystals melting at 55—56°; it is very stable towards oxidising agents, and its basic properties are so slightly developed that the hydrochloride only exists in solution, which, on evaporation, yields the original substance. The *platinochloride* forms long, prismatic needles.

Methylic 1-*paranitrophenyl*-1:2:3-*triazole*-4:5-*dicarboxylate*, prepared by the action of nitrophenylazimide on methylic acetylenedicarboxylate, crystallises from alcohol in needles melting at 117—118°. The *free* acid separates from water in white plates and needles, the latter gradually passing over into the former on standing, and melts and decomposes at 162—163°. When reduced with stannous chloride in hydrochloric acid solution, the corresponding *amido*-acid is formed, separating from water in thick, prismatic crystals melting at 218—219° when rapidly heated. It is readily oxidised by potassium permanganate in alkaline solution, yielding 1:2:3-*triazole*-4:5-*dicarboxylic acid*, $N\!\lessdot\!\begin{matrix} NH{\cdot}C{\cdot}COOH \\ \Vert \\ N{-}C{\cdot}COOH \end{matrix}$, identical with Bladin's acid (Abstr., 1893, i, 375, 1894, i, 76); this forms prismatic crystals melting and evolving carbonic anhydride at 200—201°. The *potassium hydrogen* salt forms microscopic needles containing $1H_2O$. During the oxidation, a second substance is produced in considerable amount; this separates from water in orange-red, granular crystals melting and decomposing at 328—330°, but was not further investigated.

1-*Paranitrophenyl*-1:2:3-*triazole*, obtained by heating nitrophenyl-1:2:3-triazoledicarboxylic acid at 160°, forms pale yellow, granular crystals melting at 203—204°. On reduction, it gives the corresponding *amido*-derivative crystallising in pearly flakes and melting at 138—139°.

Ethylic 1:5-*diphenyl*-1:2:3-*triazole*-4-*carboxylate*,

$$N\!\lessdot\!\begin{matrix} NPh{\cdot}CPh \\ \Vert \\ N{-\!-}C{\cdot}COOEt \end{matrix},$$

obtained by the interaction of phenylazimide and ethylic phenylpropiolate, crystallises in needles melting at 134—135°. The *free* acid is a white, crystalline substance melting at 183°. The *silver* salt is a white, amorphous mass, and the *copper* salt forms groups of truncated slender prisms.

There can be no doubt that the addition of substituted azimides to ethereal salts of the acetylenecarboxylic acids to form 1:2:3-triazole derivatives is a general reaction. A. W. C.

Some Derivatives of Caffeine. By ALFRED EINHORN and EDUARD BAUMEISTER (*Ber.*, 1898, **31**, 1138—1141).—Caffeinecarboxylamide, $\begin{matrix} NMe\cdot CO\cdot C\cdot NMe \\ CO\cdot NMe\cdot C \text{——} N \end{matrix} \gg C\cdot CO\cdot NH_2$ (Gomberg, Abstr., 1895, i, 628), reacts like caffeine itself (Maly and Andreasch, Abstr., 1883, 1016) when it is boiled with aqueous caustic soda, and yields *caffeidinedicarboxylic acid*, $\begin{matrix} COOH\cdot NMe\cdot CO\cdot C\cdot NMe \\ NHMe\cdot C \text{——} N \end{matrix} \gg C\cdot COOH + H_2O$, which melts and decomposes at 141°; when boiled with water, it loses carbonic anhydride, and forms caffeidine; its *sodium*, with $3H_2O$, and anhydrous *silver* salts were prepared and analysed.

Chlorocaffeine (1 mol.) reacts with secondary amines (2 mols.) when the two substances are heated together for 4—6 hours at 130—180° (compare Cramer, Abstr., 1895, i, 116). *Piperidyl, diethylamido-, dipropylamido-, diamylamido-*, and *dibenzylamido-caffeine*,

$$C_8H_9N_4O_2\cdot C_5NH_{10},$$

&c., melt at 142°, 109°, 95°, 99·5° and 162° respectively. *Benzylamido-caffeine*, from chlorocaffeine, benzylamine, and alcohol at 180°, melts at 231°. C. F. B.

Cinchotine. By ZDENKO H. SKRAUP (*Annalen*, 1898, **300**, 357—358. Compare O. Hesse, this vol., i, 388).—The author takes exception to certain statements made by Hesse (*loc. cit.*). He continues to call the base in question cinchotine, pointing out that the name hydrocinchonine, employed by Hesse, may give rise to confusion with the hydrocinchonines of Zorn, with none of which is the alkaloid identical. M. O. F.

Derivatives of Veratrine. By GEORGE B. FRANKFORTER (*Amer. Chem. J.*, 1898, **20**, 358—373).—The veratrine employed was composed of microscopic, imperfect, granular crystals of a light grey colour; it is slightly soluble in water and very soluble in the ordinary organic solvents, separating as a light brown varnish, which, on stirring with water, changes to a granular, semi-crystalli ne mass melting at 146—148°. It has a peculiar, bitter, rasping taste producing numbness of the tongue if taken in small quantities: is a violent sternutatory, causing intense irritation of the nasal mucous membrane, and retards the action of the heart. It has a slightly alkaline reaction, which is intensified when dissolved in alcohol. The purified substance contains $1H_2O$, and one methoxy-group, a fact which has not previously been recorded. *Veratrine tetriodide* is produced when the alkaloid is triturated with an alcoholic solution of iodine and then allowed to remain with excess of iodine for some days, as a light red, crystalline powder melting at 129—130°. When dried at 110° to a constant weight, the *triiodide* is obtained as a dark brown, amorphous substance melting at 136—138°; and when treated with dilute ammonia, it yields the *moniodide*, which separates from dilute alcohol as a fine, crystalline powder melting at 212—214°. When the tetriodide is digested with strong ammonia, the whole of the iodine is removed, with production of a white, insoluble gelatinous *substance* melting at 189°, which is not identical with the free alkaloid.

Chloralhydroveratrine, $CCl_3\cdot CH(O\cdot C_{32}H_{48}NO_8)_2$, obtained by the action of chloral on the free alkaloid, is a creamy white, crystalline powder melting at 220°, and resembles veratrine in its physiological properties.

Veratrine methiodide, produced by the action of methylic iodide on the base, separates from water as an almost white, crystalline powder, melting at 210—212° with apparent decomposition. When treated with potassium hydroxide or moist silver oxide, *veratrine methohydroxide* is obtained as a white, granular powder becoming brown when heated to 80—90°, but not finally melting until 188—190°; it is physiologically inactive. The *hydrochloride* is a light grey, very unstable, granular powder decomposing below 100°; and the *aurochloride* is a beautiful, lemon yellow, crystalline powder melting at 149°.

Veratrine ethobromide is a light yellow, amorphous mass which readily decomposes; and the *allylic iodide* is a white, crystalline powder melting at 235—236°. A. W. C.

Rotatory Power of Cocaine Hydrochloride. By HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 7, 59—61).—The author points out that the specific rotatory power of cocaine hydrochloride is often incorrectly stated to be $[\alpha]_D = -52\cdot5°$, and that this arises from a misinterpretation of Antrick's equation $[\alpha]_D = -[52\cdot18 + 0\cdot1588_q]$ (compare Abstr., 1887, 506). In his determinations Antrick employed 40 per cent. alcohol as a solvent, since he found that, with water alone, a turbidity was produced. Five samples examined by the author, however, were probably of greater purity, since they dissolved in water, giving clear solutions, three of which gave $[\alpha]_D = -71\cdot66$, whilst the remaining two gave $[\alpha]_D = -70\cdot83$; each solution contained 2 grams of the hydrochloride per 100 c.c., and was examined at 14—16°. An aqueous solution of 2·712 grams per 100 c.c. of the hydrochloride which had been recrystallised from absolute alcohol, gave $[\alpha]_D = -71\cdot94$, whilst 2 per cent. solutions in alcohol of the same concentration as that employed by Antrick gave the somewhat lower value of $[\alpha]_D = -69\cdot43$, this again being decreased by increasing the concentration, so that for an 8 per cent. solution $[\alpha]_D = -69\cdot15°$.

That the author's values are higher than those of Antrick is probably due to his having used purer samples of the hydrochloride; no melting points are, however, given. He points out, in conclusion, that the rotatory power of cocaine hydrochloride is unaffected by heating its aqueous solution during 2 hours at 100°.

W. A. D.

Alkaloids of the Yellow Lupin (*Lupinus luteus*.) By HEINRICH RITTHAUSEN (*Chem. Zeit.*, 1897, 21, 718).—The alcoholic extract of yellow lupins, after being freed from alcohol, was mixed with an equal quantity of water and 1/10 of its weight of potassium hydroxide, and then extracted three times with light petroleum. The further separation of lupinine and lupinidine was effected by Baumert's method (Abstr., 1885, 177). J. J. S.

Scopolamine. By ERNST SCHMIDT (*Arch. Pharm.*, 1898, **236**, 9—11, 47—74. Compare Abstr., 1897, i, 385).—A reply to Hesse (Abstr., 1896, i, 655; and 1897, i, 132). According to the author, an almost inactive hydrobromide may be prepared from the scopolamine contained in scopolia root if the extract is made alkaline with potassium carbonate or sodium hydroxide; whilst the ordinary hydrobromide is obtained when a weak alkali such as sodium hydrogen carbonate is used. Similarly, the commercial hydrobromide yields an inactive scopolamine when the aqueous solution is made alkaline with sodium hydrogen carbonate; the same scopolamine is also obtained by the action of silver oxide, or of a small quantity of sodium hydroxide on the ordinary scopolamine, and is identical with Hesse's atroscine.

E. W. W.

Scopolamine and Scopoline. By WALTER LUBOLDT (*Arch. Pharm.*, 1898, **236**, 11—33. Compare Abstr., 1896, i, 514).—One hundred parts of water at 15° dissolve 1·4946 parts of scopolamine. The specific rotatory power of scopolamine in aqueous solution, $[\alpha]_D = -4° 30'$, and in alcoholic solution $[\alpha]_D = -1° 37'$. The product obtained by the action for a short time of concentrated sulphuric acid on scopolamine yields an *aurochloride*, $C_{34}H_{40}N_2O_7,2HAuCl_4$, which crystallises from hot water in long needles and melts at 183—185° (uncorr.). Attempts to obtain the hydrochloride from the aurochloride by precipitating the gold with hydrogen sulphide and concentrating the filtrate, resulted only in the production of deliquescent needles which rapidly decomposed; from the solution, however, a *platinochloride*, $(C_{17}H_{19}NO_3)_2,H_2PtCl_6$, was obtained. The analogy between scopoline and tropine in regard to the products of oxidation and methylation is pointed out. According to the author, one of the atoms of oxygen contained in the molecule of scopoline probably occurs as a ketone group. E. W. W.

Scopoleines. By WALTER LUBOLDT (*Arch. Pharm.*, 1898, **236**, 33—47. Compare Abstr., 1896, i, 396).—*Salicylscopoleine*, $C_{15}H_{17}NO_4$, prepared by melting commercial salicylide with scopoline, crystallises in slender, white needles, is slightly soluble in water, easily soluble in the usual organic solvents, and gives a violet coloration with ferric chloride. The hydrochloride, hydrobromide, sulphate, aurochloride, and platinochloride were prepared and analysed. *Phenylglycolylscopoleine* (homoscopolamine), $C_{16}H_{19}NO_4$, obtained by melting scopoline with mandelic anhydride, or by heating these substances dissolved in benzene at 140°, is a syrupy liquid which could not be crystallised; the aurochloride was prepared in the form of a resinous mass and analysed. E. W. W.

Cactus Alkaloids. III. By ARTHUR HEFFTER (*Ber.*, 1898, **31**, 1193—1199. Compare Abstr., 1896, i, 267).—Pellotine not only contains two methoxy-groups, but a methyl group combined with nitrogen, and has the formula $C_{10}H_{10}O(OMe)_2NMe$. The *hydriodide* crystallises in small, yellowish prisms and is readily soluble in water.

The alkaloids of *Anhalonium Lewinii*, *Mezcaline hydrochloride*, crystallises in slender, white needles, whilst the *hydriodide* forms large, transparent plates, and the *aurochloride* long prisms. The *methiodide*,

$C_{11}H_{17}NO_3,MeI$, crystallises in colourless prisms melting at 174°, and yields a *methochloride*, the *platinochloride* of which crystallises in yellow needles. Mezcaline contains a methyl group united with nitrogen, and has the formula $C_7H_5(OMe)_3NMe$. It is converted by potassium permanganate into an *acid* which contains nitrogen, and crystallises in long, white needles melting at 169°.

Anhalonidine melts at 154°, and is optically inactive, the optical activity previously observed having been due to an impurity. The *hydrochloride*, *sulphate*, and *hydriodide* are all anhydrous and crystallise well, whilst the *aurochloride* melts at 152°. Anhalonidine, as previously stated, contains two methoxy-groups, but does not contain a methylimido-group or a hydroxyl group.

Anhalonine hydriodide forms yellowish needles, whilst the *aurochloride* is a heavy, microcrystalline powder. As a secondary base, anhalonine forms a *nitroso*-compound, $C_{12}H_{14}NO_3 \cdot NO$, which crystallises in colourless prisms melting at 59°. The base is converted by methylic iodide into *methylanhalonine hydriodide*, $C_{13}H_{17}NO_3,HI$, which forms spherical aggregates of white needles, whilst the corresponding *hydrochloride* crystallises in white needles, and forms a crystalline *aurochloride* and *platinochloride*. The free *base* crystallises from ether in thin plates, and unites with methylic iodide to form *methylanhalonine methiodide*, which melts at 210° and yields a *methochloride*, the *platinochloride* of which crystallises in needles.

Lophophorine has hitherto only been obtained as an oil, and in very small amount. The *hydrochloride*, $C_{13}H_{17}NO_3,HCl$, is optically inactive, and crystallises in microscopic needles. The base does not contain a methylimido-group, and is isomeric with methylanhalonine.

A. H.

What is Osborne's Diastase? By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1898, 31, 1127—1130).—A reply to Osborne (this vol., i, 286).

C. F. B.

Chemical Nature of the Amylolytic Ferments. By AUGUSTIN WRÓBLEWSKI (*Ber.*, 1898, 31, 1130—1136).—*Diastase.*—When ammonium sulphate was added to an aqueous solution of impure diastase, a turbidity was produced when the solution contained about 50 per cent. of the sulphate and flakes of araban separated. More ammonium sulphate was then added until 60 per cent. was present; the precipitate then produced was a mixture of the pentosan with diastase. The second filtrate was saturated with ammonium sulphate; the precipitate now formed consisted of diastase only; 1 drop of a solution of it acted so vigorously on 0·1 gram of soluble starch, that after 2—3 minutes a blue colour could be obtained no longer with iodine. A specimen of this diastase was purified by dissolving it in water, separating it from ammonium sulphate by dialysis of the solution, and precipitating it with alcohol and ether; it contained 16·53 per cent. of nitrogen after this treatment. An aqueous solution of this diastase is not coagulated by boiling, even when acetic or hydrochloric acid in not too large amount has been added. It is precipitated by tannic acid, but the precipitate is soluble in very weak alkali, and this solu-

tion retains the power of hydrolysing starch. Diastase is a proteid, and is most nearly allied to the proteoses.

Takadiastase.—This substance, obtained by cultivating the fungus *Aspergillus oryzæ* on wheat chaff, contains 44 per cent. of ash, chiefly phosphates; the rest consists of carbohydrates, proteids, and other substances. It was digested in water in the cold, the filtered solution was precipitated with alcohol, and the precipitate dissolved in water and treated much as above. A yellow substance was obtained eventually; it hydrolysed starch, and had the character of a proteid.

Invertin.—This substance, obtained from yeast, was separated from carbohydrates in the same way as takadiastase. One drop of its solution inverted 3 grams of cane-sugar in 3 minutes at 38°; it has the character of a proteid.

C. F. B.

Oxyproteic Acid, a New Constituent of Urine. By STANISLAS BONDZYŃSKI and RUDOLF GOTTLIEB (*Chem. Centr.*, 1897, ii, 619—620; from *Centr. med. Wiss.*, 35, 578—580).—The barium salt of *oxyproteic acid*, $C_{43}H_{82}N_{14}O_{31}S$, is prepared from human or dogs' urine by adding 10 c.c. of 20 per cent. sulphuric acid to each litre of the concentrated syrupy urine and then 5 times the volume of alcohol, the filtrate is diluted with water, heated with barium hydroxide in excess, the barium removed by carbonic anhydride, the alcohol evaporated, the solution filtered, the filtrate concentrated, and then poured into 4 or 5 times its volume of alcohol. The flocculent precipitate so obtained is purified by dissolving in water and again precipitating with alcohol. In order to further purify the salt, the author makes use of the property which the acid possesses of being precipitated by mercuric nitrate or sulphate. The *barium* salt is a white, hygroscopic powder, is very soluble in water and insoluble in absolute alcohol. Salts of the alkalis and heavy metals could not be obtained in a pure state. Oxyproteic acid is obviously an oxidation product of albumin, and is probably analogous to the substance obtained by Maly by oxidising egg-albumin with permanganate, and to Schmiedeberg's oxyalbuminic acid. The acid, which was not obtained in the free state, neither gives the xantho-protein test nor the biuret reaction, and is not precipitated by phosphotungstic acid or by mercuric chloride. With Millon's reagent it gives a faint chamois-yellow coloration. The sulphur is not contained in the acid in a form which can easily be eliminated. No tyrosine is obtained by the action of sulphuric acid.

Mercuric nitrate precipitates from the urine of dogs which have been abundantly fed on flesh about 2·5 per cent. of the total nitrogen as oxyproteic acid, and the quantity of acid calculated from the barium salt amounts to about 10 grams per litre of urine. In human urine, 2—3 per cent. of the total nitrogen is in the form of this acid, and about 3—4 grams are eliminated in 24 hours. In cases of phosphorus poisoning in dogs, the amount of this acid increases considerably.

E. W. W.

So-called Oxyproteic Acid, a Constituent of Urine. By GUSTAV TÖPFER (*Chem. Centr.*, 1897, ii, 956—957; from *Centr. med. Wiss.*, 35, 705—707).—Bondzyński and Gottlieb's oxyproteic acid

(preceding abstract) is identical with the substance prepared by the author (*Wien. klin. Woch.*, 1892, No. 3) from urine, by precipitating with phosphotungstic acid, then removing this acid with barium hydroxide, and finally precipitating the barium compound with alcohol, or by treating the urine with copper sulphate and alkali or baryta and then precipitating the barium salt with alcohol. According to the author, Bondzyński and Gottlieb have over-estimated the amount of this substance present in urine as their barium precipitate contained uric acid, creatinine and xanthine substances, and they are also wrong in stating that this substance has been hitherto determined as urea, for by Mörner and Sjöqvist's method it is separated from the urea. This acid is precipitated by alcoholic mercuric chloride, but not by tannic acid or by potassium mercury iodide. E. W. W.

Sulphur in Proteids. By FRIEDRICH N. SCHULZ (*Zeit. physiol. Chem.*, 1898, **25**, 16—35).—It is well known that the sulphur in proteids is partly removable by boiling with alkali, and partly not so. The proportion between these amounts is variously given by different observers. In the present research, the method used is a modification of Fleitmann's in which metallic zinc is added to the boiling alkali to prevent oxidation.

Treated in this way, thioacetic acid and thiourea yield the whole of their sulphur; thiosulphates, cystin, and cystein yield about half.

The following results (given in percentages) were obtained with proteids; in the case of the three first named, the proteid used was in the crystalline condition. With the exception of the egg-albumin, the preparations were made from horses' blood.

	Serum-albumin.	Egg-albumin.	Hæmoglobin.	Globin.	Serum-globulin.
Total sulphur (a)	1·89	1·18	0·43	0·42	1·38
Sulphur removable by potash (b)	1·28	0·49	0·19	0·2	0·63
a : b	3 : 2·03	2 : 0·83	2 : 0·88	2 : 0·95	2 : 0·91

W. D. H.

Cleavage Products of Proteids. I. Constituents of Witte's Peptone. By OTTO FOLIN (*Zeit. physiol. Chem.*, 1898, **25**, 152—164). —From Witte's 'peptone' pure protoalbumose may be prepared by precipitating the heteroalbumose by dialysing away the salts. From the filtrate, protoalbumose is precipitated as its copper compound, from which the copper is subsequently removed; it agrees in its properties with Kühne's protoalbumose. By lead acetate, it is broken up into two substances, one of which is similar to, or identical with, Meissner's meta-peptone or Kühne's acro-albumose; the second substance is present in smaller quantities and has yet to be investigated. After the removal of the protoalbumose, the last traces of which are got rid of by the addition of alcohol, saturation with ammonium sulphate precipitates the deuteroalbumose. This substance when pure is

free from the loosely combined sulphur which blackens lead acetate In fact, the amount of sulphur altogether is so small (0·25 per cent.) that it may be due to contamination with impurities.

The so-called true peptone in Kühne's sense is regarded as non-existent, but as a mere residue of albumoses. This view has been previously expressed by Pekelharing (*Centr. f. Physiol.*, 7, 43).

W. D. H.

Action of Halogens on Proteids. By F. GOWLAND HOPKINS and STANISLAW N. PINKUS (*Ber.*, 1898, **31**, 1311—1326).—Proteids in solutions of 0·6—5·0 per cent. strength absorb bromine readily at the ordinary temperature; no noticeable rise of temperature occurs, and the bromine is simply absorbed at first; only when excess has been added does a precipitate separate. In the case of protoalbumose and deuteroalbumose, the temperature must not exceed 5° during bromination, otherwise the precipitate forms resinous lumps.

The reaction has been studied in greatest detail in the case of egg-albumin. This substance absorbs chlorine and iodine also; in the last case a temperature of 35—40° is necessary in order to produce a precipitate. The halogen acid formed can take no part in the reaction, for the same products are obtained with bromine and chlorine when potassium bromate or chlorate respectively is present, in which case no halogen acid can be formed. The original precipitate obtained with bromine contains 14·04 per cent. Br; after dialysis, 10·54. Three ways of purifying it were adopted, each way leading to a different product. (I) It was dissolved in 1 per cent. sodium carbonate solution, precipitated with 2 per cent. acetic acid, dialysed, washed with alcohol and ether, and dried under diminished pressure; it then formed a yellowish, amorphous powder; percentage of Br, 3·84—4·02 in different samples. (II) It was dissolved in hot alcohol and the solution run into cold ether, the precipitate was washed with ether and dried, when it formed a yellowish, amorphous powder containing Br, 10·69—10·98 per cent. (III) It was dissolved in alcohol, and bromine was added to this solution, which was then run into ether containing bromine; the precipitate was washed with ether and dried; it formed a reddish-white, amorphous powder, Br, 14·82—15·01. Any of the three products can be converted into the others by treating it in the way by which the latter were obtained. The mean percentage of bromine is quoted below, as also that of chlorine and iodine in products prepared by similar methods; it will be noticed that these numbers stand to each other roughly in the ratio of the atomic weights of the respective halogens, which indicates a similarity of constitution in the products.

	Chlorine.	Bromine.	Iodine.
Group I.	1·89 per cent.	3·92 per cent.	6·28 per cent.
Group II.	3·60 „	10·82 „	17·94 „
Group III.......	6·07 „	14·91 „	—

These products in all cases form a horny mass, resembling dried white of egg, when they are dried slowly. They intumesce and carbonise at 160—200°, evolving halogen acid; they have an astringent, bitter taste; they do not dialyse, either from dilute alkaline or from

alcoholic solution; they give the xanthoprotein and biuret reactions, but not Millon's or Adamkiewicz's; they are pronounced acids, displacing carbonic acid, and they form insoluble salts with heavy metals; when submitted to digestion, they yield substances which dialyse, have the character of peptones, and contain halogen; the pancreatic digestion is rapid, but the peptic is slow, on account of the very slight solubility of the substances in acids.

As method III gave the most concordant results, it was adopted for further work. A number of proteids were treated by this method; the results are tabulated below.

Protein.	Method of preparing the proteid.	Bromine.	Ash.
		Per cent.	Per cent.
Egg-albumin.......	Diluted with water	15·00	—
Cryst. ,, ...			
Fraction 1.......	According to Hofmeister	15·29	—
,, 2.......	According to Hofmeister	16·48	—
,, 3.......	According to Hofmeister	15·67	—
,, 4.......	According to Hofmeister	12·64	—
,, 5......	According to Hofmeister	12·79	—
Serum-albumin 1.	Fractionated with $(NH_4)_2SO_4$, end fraction	12·61	—
2.	Salted out with $(NH_4)_2SO_4$..........	12·15	—
3.	According to Hammarsten	12·94	—
Serum-globulin 1.	Half-saturated with $(NH_4)_2SO_4$.....	14·03	—
2.	Saturated with $MgSO_4$	13·92	0·732
3.	Precipitated by diluting with water.	13·53	—
Casein	Dissolved in ammonia, precipitated with acetic acid........................	11·17	—
Protoalbumose	(Grübler)	16·30–17·12	—
Deuteroalbumose.	(Grübler)	17·63	—

C. F. B.

Production of a Mucinoid Substance by Bacteria. By Albert Charrin and Alexandre Desgrez (*Compt. rend.*, 1898, **126**, 596—598).—When *Bacillus pyocyanicus* is cultivated in beef broth prepared in the usual way, the liquid often becomes viscous and yields a precipitate with alcohol, acetic acid, inorganic acids, sodium chloride, and magnesium sulphate, which is soluble in excess of the inorganic acids, and also dissolves in solutions of alkali hydroxides or carbonates. Its formation depends on the presence of beef extract, but has no relation to the production of pyocyanin. The precipitate produced by alcohol swells up in water and forms a pseudo-solution which can pass through a filter; it contains sulphur, and in general characters resembles the mucinoids. A solution in dilute sodium carbonate solution when injected subcutaneously into the ear of a rabbit, produces diarrhœa and intramuscular hæmorraghia, resulting in death. The formation by bacteria of a substance analogous to those produced by the cells of higher organisms is of special interest, and may play an important part in inflammations of the mucous membrane. Other bacteria seem to have the same power as *Bacillus pyocyanicus*.

C. H. B.

Organic Chemistry.

Some Aliphatic Nitro-compounds. By LOUIS HENRY (*Rec. Trav. Chim.*, 1898, **17**, 1—26).—*Nitroethylic alcohol*, $NO_2\cdot CH_2\cdot CH_2\cdot OH$, which cannot be obtained by the partial condensation of formaldehyde with nitromethane (compare this vol., i, 5), is conveniently prepared by dissolving ethylenic iodhydrin (86 grams) in three times its volume of ether, and leaving the solution in contact with silver nitrite (90 grams) during $1\frac{1}{2}$ hours at the ordinary temperature, the mixture finally being gently heated. A similar method was adopted by Meyer and Demuth (Abstr., 1889, 360; 1890, 857), but on account of their employing impure ethylenic iodhydrin, they were unable to obtain a product having a definite boiling point. Nitroethylic alcohol is a colourless liquid, with a pungent odour and sharp taste, which boils at 119—120° under a pressure of 35 mm., and at 194°, with slight decomposition, under a pressure of 765 mm.; it has a sp. gr. = 1·270 at 15°, its vapour density is 3·06 (calc. 3·14), and it does not solidify at – 80°.

Nitropropylene, $CH_2{:}CH\cdot CH_2\cdot NO_2$, prepared by leaving a cooled ethereal solution of allylic bromide in contact with silver nitrite during $1\frac{1}{2}$ hours, and subsequently fractionating the product under reduced pressure, is a colourless, mobile liquid, with a pungent odour similar to that of allylic bromide, and a bitter taste; it has a sp. gr. = 1·051 at 21°, the vapour density is 3·08 (calc. 3·00), and it boils at 87—89° under a pressure of 180 mm., and at 125—130° under 760 mm.; in the latter case, an explosion generally occurs when the temperature reaches 130°. It is evident, from the properties given, that the nitropropylene described by Meyer and Askenasy (Abstr., 1892, i, 1062) was highly impure.

aa-Chloronitroethane, prepared by passing chlorine into nitroethane dissolved in a slight excess of moderately concentrated caustic soda, or by adding the latter solution to carbon tetrachloride saturated with chlorine, is a colourless liquid which boils at 124—125° (758 mm.), has a sp. gr. = 1·247 at 7·5°, a vapour density = 3·63 (calc. 3·78), and is soluble in alkalis; it condenses readily with formaldehyde, $\beta\beta$-chloronitropropylic alcohol (this vol., i, 5) being obtained.

aβ-Chloronitroethane, $CH_2Cl\cdot CH_2\cdot NO_2$, formed together with its isomeride, chlorethylic nitrite, on heating ethylenic chloriodide with an excess of silver nitrite, is a colourless liquid which boils at 105° under a pressure of 72 mm., and at 173—174° under the ordinary pressure; its sp. gr. = 1·405 at 7°, and its vapour density = 3·54 (calc. 3·78).

Of the five possible chloronitropropanes, the compounds

$$NO_2\cdot CH_2\cdot CHCl\cdot CH_3$$

and $CH_2Cl\cdot CH_2\cdot CH_2\cdot NO_2$ have already been described; the latter (Abstr., 1897, i, 1), on being heated in a closed vessel with concentrated hydrochloric acid, yields hydroxylamine hydrochloride, and β-chloropropionic acid, which melts at 40—41°. The compound $CH_2Me\cdot CHCl\cdot NO_2$ is described in the following abstract, whilst that

having the formula $CH_2Cl\cdot CHMe\cdot NO_2$ is formed by the action of phosphorus pentachloride on the corresponding alcohol, $OH\cdot CH_2\cdot CHMe\cdot NO_2$; it is a colourless liquid which is insoluble in water, and boils at 170—174° under a pressure of 155 mm., and at 94° under 46 mm.; its sp. gr. = 1·200 at 18°. *ββ-Chloronitropropane*, $CH_3\cdot CMeCl\cdot NO_2$, prepared by passing chlorine into secondary nitropropane dissolved in an equivalent quantity of aqueous potassium hydroxide, is a colourless liquid, with an agreeable odour, and is insoluble in water, but soluble in alcohol or ether; it boils at 133—134° (758 mm.), has a vapour density = 4·12 (calc. 4·26), and a sp. gr. = 1·179 at 16°. As a consequence of its structure, it neither dissolves in alkalis nor condenses with aliphatic aldehydes.

Tetrachloronitropropane, $CCl_3\cdot CHCl\cdot CH_2\cdot NO_2$, prepared by the action of phosphorus pentachloride on the corresponding trichloronitroisopropylic alcohol, is a somewhat viscous liquid, with an odour resembling that of chloropicrin; it boils at 108—109° under a pressure of 28 mm., at 199—200° under 767 mm.; and has a sp. gr. = 1·580° at 11°, and a vapour density = 7·70 (calc. 7·84).

In conclusion, the author discusses the relation between the boiling point and structure of a number of halogen-substituted nitroparaffins. W. A. D.

Derivatives of Primary Nitropropane. By J. PAUWELS (*Rec. Trav. Chim.*, 1898, **17**, 27—49).—Primary nitropropane is best prepared (compare V. Meyer and Rilliet, this Journal, 1873, 261) by gradually adding normal propylic iodide to finely powdered silver nitrite suspended in ether, and finally heating for a short time on the water bath; it boils at 130—131° under a pressure of 765 mm., and has a sp. gr. = 1·009 at 12°, and = 0·9999 at 16·5°. On mixing nitropropane (1 mol.) with an aqueous solution of formaldehyde (1 mol.) and adding a small piece of potassium carbonate, rapid combination takes place, *secondary nitro-normal butylic alcohol*, $NO_2\cdot CHEt\cdot CH_2\cdot OH$, being formed; this is a nearly colourless liquid, with a pungent odour and bitter taste; it boils at 127—130° under 35 mm. pressure, has a sp. gr. = 1·1365 at 11·5°, and dissolves somewhat sparingly in water, but easily in alcohol, ether, and acetic acid. The vapour density is 2·60, instead of 4·11, owing probably to dissociation; the molecular weight, however, determined by the cryoscopic method, using water and acetic acid as solvents, is normal. The *sodium* derivative, $NO_2\cdot CNaEt\cdot CH_2\cdot OH$, of the alcohol is a white substance, insoluble in alcohol, but easily soluble in water; the *silver* salt, precipitated from the latter solution by silver nitrate, is a white powder soluble in ammonia; the *mercurous* salt is greyish-white, the *copper* salt green, and the *mercuric* and *ferric* salts red.

Since nitrobutylic alcohol contains the group $\vdots CH\cdot NO_2$, it readily condenses with formaldehyde (1 mol.) to form a *glycol* (2-*methylol*-2-*nitro*-1-*butanol*), $NO_2\cdot CEt(CH_2\cdot OH)\cdot CH_2\cdot OH$; the same product can also be obtained directly from nitropropane by condensation with 2 mols. of formaldehyde. It crystallises in white needles, melts at 57—58°, and is easily soluble in water, alcohol, and ether.

Nitrobutylic alcohol readily reacts with phosphorus pentachloride

to form 2-*nitro*-1-*chlorobutane*, $NO_2\cdot CHEt\cdot CH_2Cl$, a highly refractive, greenish-yellow liquid, which boils and partially decomposes at 190° (760 mm.), and has a sp. gr. = 1·165 at 21°, and a vapour density = 4·82 (calc. 4·75). *Nitrobutylic nitrate*, $NO_2\cdot CHEt\cdot CH_2\cdot NO_3$, is a yellowish, somewhat viscous liquid, which has a sp. gr. = 1·242 at 15·5°. *Nitrobutylic acetate*, $NO_2\cdot CHEt\cdot CH_2\cdot OAc$, boils at 130° under 35 mm. pressure, and has a sp. gr. = 1·0807 at 21°, and a vapour density = 6·19 (calc. 5·56).

Methyl-β-nitropropylcarbinol, $NO_2\cdot CHEt\cdot CHMe\cdot OH$, obtained by the condensation of primary nitropropane with acetaldehyde, is a colourless liquid which is soluble in water, alcohol, and ether, and boils at 120° under 37 mm. pressure, and at 130° under a pressure of 54 mm.; it has a sp. gr. = 1·075 at 15·5°, and its vapour density is 4·34 (calc. 4·59).

αα-Chloronitropropane, $NO_2\cdot CHEtCl$, prepared by passing chlorine through a solution of primary nitropropane in an equivalent quantity of aqueous caustic potash, is a colourless, mobile liquid which boils at 141—143° (761 mm.), and has a sp. gr. = 1·205 at 15°, and a vapour density = 4·26 (calc. 4·27). It condenses readily with formaldehyde, forming *ββ-chloronitrobutylic alcohol*, $OH\cdot CH_2\cdot CCl(NO_2)\cdot CH_2Me$, a colourless, viscous liquid, which boils at 145—150° under a pressure of 76 mm., has a sp. gr. = 1·229 at 15°, a vapour density = 5·13 (calc. 5·30), and is easily soluble in water, alcohol, and ether.

W. A. D.

Derivatives of Primary Nitroisobutane. By ANTOINE SHAW (*Rec. Trav. Chim.*, 1898, **17**, 50—65).—When isobutylic iodide is left at the ordinary temperature with a slight excess of silver nitrite, a yield of 50—70 per cent. of the calculated quantity of primary nitroisobutane, $NO_2\cdot CH_2\cdot CHMe_2$, is obtained; if, however, isobutylic bromide is employed, and the mixture heated, the yield is only 25—30 per cent. of the nitro-compound, 50 per cent. of isobutylic nitrite being formed. *Primary nitroisobutane* has a sp. gr. = 0·9870 at 15°; on passing chlorine through its solution in aqueous caustic potash, it is converted into *αα-chloronitroisobutane*, $NO_2\cdot CHCl\cdot CHMe_2$, a colourless mobile liquid, which boils at 151—152° (750 mm.), has a sp. gr. = 1·147 at 13°, a vapour density = 4·58 (calc. 4·74), and is insoluble in water but easily soluble in ether and alcohol.

β-Nitroisobutylcarbinol, $OH\cdot CH_2\cdot CHPr^{\beta}\cdot NO_2$, prepared by adding a small piece of potassium carbonate to a mixture of nitroisobutane and aqueous formaldehyde in molecular proportion, is a colourless liquid which boils at 138—139° under a pressure of 38 mm., has a sp. gr. = 1·0966 at 13°, a vapour density = 4·12 (calc. 4·19), and is sparingly soluble in water, but easily in alcohol and ether. The *sodium* derivative, $C_5H_{10}NO_3Na$, forms white, deliquescent crystals, the *copper* derivative is green, the *mercurous* derivative greyish-black, and the *tin*, *silver*, and *barium* derivatives white. *αβ-Chloronitroisopentane*, $CH_2Cl\cdot CHPr^{\beta}\cdot NO_2$, prepared by the action of phosphorus pentachloride on β-nitroisobutylcarbinol, is a colourless liquid which is insoluble in water, soluble in alcohol and ether, boils at 163—170° (758 mm.), and has a sp. gr. = 1·0416 at 15°, and a vapour density

= 5·09 (calc. 5·23). The *acetate* of β-nitroisobutylcarbinol, prepared by heating the latter with acetic anhydride, is a yellowish liquid which boils at 159—168° under a pressure of 38 mm., and has a sp. gr. = 1·0896 at 13°. The corresponding *nitrate*, $NO_2\cdot CHPr^{\beta}\cdot CH_2\cdot NO_3$, has a sp. gr. = 1·2373 at 15°.

A *glycol*, $NO_2\cdot CPr^{\beta}(CH_2\cdot OH)_2$, is formed by the condensation of primary nitroisobutane with two molecules of formaldehyde, or, more conveniently, by condensing 1 mol. of the latter with β-nitroisobutylcarbinol; it crystallises from water, on slow evaporation, in white plates, and has a normal molecular weight in aqueous solution.

Methyl-α-nitroisobutylcarbinol, the condensation product of nitroisobutane with acetaldehyde, has already been described (this vol., i, 5).

$\beta\beta$-Chloronitroisobutylcarbinol, $OH\cdot CH_2\cdot CClPr^{\beta}\cdot NO_2$, prepared from $\alpha\alpha$-chloronitroisobutane, $NO_2\cdot CHClPr^{\beta}$, and formaldehyde, is a colourless liquid which boils at 153° under a pressure of 36 mm., has a sp. gr. = 1·2587 at 13°, a vapour density = 5·73 (calc. 5·77), and is insoluble in water, but soluble in alcohol and ether.

Attempts to prepare definite substances by condensing acraldehyde with the nitroparaffins failed, products being obtained which could neither be crystallised nor distilled. W. A. D.

Glycol and Aldol from Isobutaldehyde and Isovaleraldehyde. By Moriz Lilienfeld and Siegfried Tauss (*Monatsh.*, 1898, 19, 61—76. Compare next abstract).—The glycol, $C_9H_{20}O_2$, prepared according to Swoboda and Fossek's directions (Abstr., 1891, 31), is a crystalline substance melting at 79—80°, and boiling at 231—232° under atmospheric pressure, or 135° under a pressure of 16 mm. When oxidised with potassium permanganate in neutral solution, it yields a crystalline *hydroxy*-acid, $C_9H_{18}O_3$, melting at 69—70°, and probably also isopropyl isobutyl ketone. When the hydroxy-acid is oxidised with potassium permanganate in acid solution, or when heated with dilute sulphuric acid in sealed tubes for 8 hours at 140—150°, it is converted into a mixture of isobutyric and isovaleric acids. This supports Lieben's statement (*Monatsh.*, 1897, 18, 76, 85) that the substance is a primary secondary β-glycol, and not a disecondary glycol.

Swoboda and Fossek (*loc. cit.*), by the action of sulphuric acid, obtained from the glycol two isomeric substances, the one of higher boiling point having a molecular weight twice as great as that of the one of lower boiling point. The authors find that oxidation of the latter with potassium permanganate or dichromate gives no satisfactory clue as to its nature, for working under very varying conditions they obtained only small amounts of volatile acids, acetone, and unchanged material.

The substance of higher boiling point is completely charred when heated in sealed tubes with sulphuric acid for 8 hours at 120—140°.

A mixture of isobutaldehyde and isovaleraldehyde, when treated with a saturated solution of potash, or when fused with potash, yields a thick syrupy liquid which cannot be distilled, as it at once splits up into a mixture of the two aldehydes, as it also does on treatment with sodium acetate. The substance, probably an *aldol*, is colourless, insoluble in water readily soluble in alcohol and ether, and does not

solidify when cooled in a freezing mixture. It reacts with hydroxylamine to form a very thick, colourless oil, probably the *oxime*, $C_9H_{19}NO_2$, boiling at 150—152° under a pressure of 20 mm.

The aldol is not acted on by aluminium amalgam, but when treated with potassium permanganate, yields the hydroxy-acid, $C_9H_{18}O_3$, alluded to above. A. W. C.

Aldol and Glycol from Isobutaldehyde and Acetaldehyde. By MORIZ LILIENFELD and SIEGFRIED TAUSS (*Monatsh*, 1898, **19**, 77—89. Compare preceding abstract).—The substance prepared by Swoboda and Fossek (Abstr., 1891, 31) by the condensation of acetaldehyde and isobutaldehyde and then termed methylisopropylethyleneglycol, is now shown to be a primary secondary β-glycol. The condensation, which does not take place readily, yields from 2—10 per cent. of the *glycol*, $C_6H_{14}O_2$, as a thick liquid boiling at 118° under a pressure of 21 mm. or 208° (uncorr.) at atmospheric pressure. It does not solidify in a freezing mixture, although Fossek expressly states that it does solidify when cooled to 0°. By the action of aqueous potash on a mixture of acetaldehyde and isobutaldehyde, an *aldol*, $C_6H_{12}O_2$, is formed as a thick, colourless liquid, with pleasant odour and bitter taste, boiling at 88—90° under a pressure of 22 mm.; it could not be made to solidify. When heated with sodium acetate in sealed tubes at 80—90° for some hours, it is converted into isobutaldehyde and crotonaldehyde. It yields an *oxime* as a colourless, thick liquid with a peculiar and characteristic odour; it boils at 137—139° under a pressure of 19 mm., and, when heated with acetic anhydride, yields the *monacetyl* derivative of the corresponding *nitrile* as a colourless liquid boiling at 105° under a pressure of 16 mm. When hydrolysed with concentrated potash, a *hydroxy*-acid, $C_6H_{12}O_3$, is produced as a yellowish oil with a strong acid reaction.

The aldol is readily oxidised by potassium permanganate, giving the same hydroxy-acid, and also methyl isopropyl ketone; on reduction with aluminium amalgam, the glycol, $C_6H_{14}O_2$, is produced. When the glycol is treated with dilute or concentrated sulphuric acid, an oil smelling like camphor is obtained, which, on distillation, yields two fractions boiling at 103—105° and 210°. The substance of lower boiling point is probably trimethyltrimethylene oxide, but no definite results have so far been arrived at. A. W. C.

Glycerol Compounds of Copper with Alkali Metals. By FRIEDRICH BULLNHEIMER (*Ber.*, 1898, **31**, 1453—1457).—A compound, $2C_3H_5O_3CuNa + EtOH + 9H_2O$, was prepared by mixing 5 grams of copper hydroxide, 15 c.c. of water, 2·5—3 grams of glycerol, and 3 grams of pure caustic soda, allowing the mixture to remain in a closed vessel till a solution had been formed, adding 50 c.c. of alcohol (96 per cent.), filtering, adding more alcohol (about 30 c.c.) until a turbidity appeared, and then allowing to remain. The compound crystallises in small but long prisms, blue in colour; at 100°, under diminished pressure, it loses alcohol and water, $2C_3H_5O_3CuNa + 3H_2O$ remaining (the substance analysed was dried under diminished pressure, but in the absence of a drying agent); it absorbs carbonic anhydride from the air, copper carbonate being formed.

Another compound, $C_3H_5O_3CuNa + 3H_2O$, was obtained by dissolving 3 grams of copper nitrate in 1 gram of glycerol and 2 c.c. of water, diluting to 100 c.c. with alcohol (96 per cent.), warming to 70°, adding 5 c.c. of a solution of 2·5 grams of caustic soda in water, shaking for a little while, pouring off the hot, nearly clear deep blue solution from the dark green, slimy deposit, and allowing it to remain in a closed vessel. It crystallises in blue, hexagonal plates, with an angle of about 60°; it absorbs carbonic anhydride and water from the air; its solution in water deposits cupric oxide when boiled.

A compound, $C_3H_5O_3CuLi + 6H_2O$, was obtained by dissolving 4 grams of lithium hydroxide in a hot mixture of 60 c.c. water and 60 c.c. alcohol (96 per cent.), adding a solution, saturated at 60°, of copper acetate in 25 c.c. water, 50 c.c. alcohol, and 2 grams of glycerol, filtering the hot solution, diluting it with 200 c.c. alcohol and 60—80 c.c. ether, and allowing it to remain at 0°. The compound crystallises in elongated, hexagonal plates. C. F. B.

The Glucoses formed from Chagual Gum. By ERNST WINTERSTEIN (*Ber.*, 1898, **31**, 1571—1573).—Chagual gum, the product of a monocotyledonous plant, dissolves in water to a large extent; the solution is only feebly dextrorotatory, and does not reduce Fehling's solution. When oxidised with nitric acid of sp. gr. = 1·15, the gum yields 21 per cent. of mucic acid; when distilled with 12 per cent. hydrochloric acid, it yields 24 per cent. of furfuraldehyde; it must, then, be capable of yielding 28·5 per cent. of galactose, and 45 per cent. of pentose. The best yield of carbohydrates was obtained by boiling the gum for 4—5 hours with 5 per cent. sulphuric acid in a reflux apparatus; the portion of the product more soluble in strong alcohol was xylose, the less soluble portion appeared to be a mixture of *i*-galactose with a little *d*-galactose. C. F. B.

Double Salts containing Selenium. By JAMES F. NORRIS (*Amer. Chem. J.*, 1898, **20**, 490—508).—Selenium tetrachloride is decomposed by water even in presence of strong hydrochloric acid, and is incapable of forming double salts with ammonium chloride. Muthmann and Schäfer have shown that the only double compound obtainable with selenium and ammonium chloride has the composition $2SeO_2,NH_4Cl + 2H_2O$ (Abstr., 1893, ii, 318). In the case of double salts containing dimethylamine and trimethylamine, the author finds that the introduction of the alkyl groups has a marked influence on the stability of the selenium haloids, and that salts containing $SeOCl_2$ are capable of existence.

Salts with Trimethylamine.—The *salt* $SeOCl_2,NMe_3,HCl$, prepared by mixing a strong hydrochloric acid solution of trimethylamine with excess of selenium tetrachloride, can be obtained in well-defined, colourless, monoclinic plates; it is hygroscopic and very soluble in water, hydrochloric acid, and alcohol.

The *salt* $SeOCl_2,SeO_2,2NMe_3,HCl + H_2O$, obtained from the preceding salt by recrystallising it from alcohol and ether containing no hydrochloric acid, forms colourless, semi-transparent plates.

In making these chlorides, selenium dioxide and hydrochloric acid may be employed instead of the tetrachloride.

The *salt* $SeBr_4,SeOBr_2,2NMe_3,HBr$, obtained by mixing selenium tetrabromide with trimethylamine hydrobromide, dissolved in dilute hydrobromic acid and evaporating the solution, crystallises in long, red needles or in deep red orthorhombic crystals; it is stable in a dry atmosphere.

The *salt* $SeBr_4,2NMe_3,HBr$ is obtained when a solution containing an excess of trimethylamine hydrobromide is evaporated, rejecting the crystals first formed; it forms large, red octahedra. The corresponding double haloids of ammonium, potassium, and rubidium with selenium bromide also crystallise in octahedra. The first crop referred to above also contains greenish-brown needles, which are probably those of another double bromide which has not hitherto been obtained pure.

The *salt* $SeBr_4,2(NMe_3,HBr_2)$ crystallises in stout, dark-red needles when bromine is added to a hot saturated solution containing 1 molecular proportion of selenium tetrabromide and two of trimethylamine hydrobromide in dilute hydrobromic acid. Two atomic proportions of bromine are liberated when it is dissolved in water.

The *salt* $SeBr_4,2(NMe_3,HBr_2),NMe_3$ separates in red crystals when a solution containing selenium tetrabromide, bromine, and a large excess of trimethylamine hydrobromide is allowed to evaporate; it also loses bromine when dissolved in water.

Salts with Dimethylamine.—The *salt* $2SeOCl_2,3NHMe_2,HCl$ is deposited in monoclinic crystals from a solution containing 2 molecular proportions of selenium tetrachloride (or selenium dioxide) and one of dimethylamine hydrochloride in strong hydrochloric acid; it is deliquescent, and dissolves readily in water, alcohol, and hydrochloric acid.

The *salt* $SeO_2,NHMe_2,HCl$ is obtained in stout, colourless prisms when a solution of the preceding salt is crystallised from alcohol and ether. Dimethylamine resembles ammonia in forming a double salt containing selenium dioxide; the corresponding trimethylamine salt does not exist.

The *salt* $2SeBr_4,SeBr,3NHMe_2,HBr$ crystallises in dark-brown, diamond-shaped plates when a concentrated hydrobromic acid solution containing dimethylamine hydrobromide and excess of selenium tetrabromide is evaporated. The salt is decomposed by water with the liberation of selenium, and probably contains the elements of selenium monobromide, which is similarly decomposed in aqueous solutions.

The *salt* $SeBr_4,2(NHMe_2,HBr)$ crystallises in bright red, prismatic needles when a dilute hydrobromic acid solution of selenium tetrabromide and dimethylamine hydrobromide is evaporated. This compound can be obtained in monoclinic or triclinic prisms, whereas the other bromides of the type $SeBr_4,2MBr$, containing potassium, rubidium, ammonium, and trimethylammonium, crystallise in octahedra. A third bromide crystallising like the trimethylamine compound in green needles is produced, but cannot be purified.

The *salt* $SeBr_4,2(NHMe_2,HBr_2)$, prepared like the corresponding trimethylamine double salt, crystallises in dark red needles.

The *salt* $SeBr_4,2(NHMe_2,HBr_2),NHMe_2,HBr$ crystallises in deep brown prisms on adding bromine to a saturated solution of selenium tetrabromide and excess of dimethylamine hydrobromide in strong hydrobromic acid.

G. T. M.

Preparation of a Synthetic Methylheptenone. By Georges Leser (*Bull. Soc. Chim.*, 1897, [iii], 17, 108—110).—Tiemann and Krüger (Abstr., 1895, i, 645) were unable to isolate the methylheptenone, $CHMe_2\cdot CH_2\cdot CH{:}CH\cdot COMe$, obtained by Barbier and Bouveault (Abstr., 1894, i, 224) by the condensation of isovaleraldehyde with acetone, and stated that the principal product of the reaction was di-isovaleraldehyde, boiling at 190°. The author finds, however, that if a mixture of isovaleraldehyde (1 part), acetone (1 part), sodium hydroxide solution (1 : 10 ; 1 part), and water (3 parts) is kept in constant agitation for about 12 hours, and the supernatant liquid subjected to repeated fractional distillation, the methylheptenone boiling at 180° (corr.) is easily obtained in quantity, whilst the portion boiling above 180° is relatively small in amount. N. L.

Action of Sodium on Ethylic Dimethylacetoacetate. By Max Conrad and Richard Gast (*Ber.*, 1898, 31, 1339—1344).—Ethylic malonate containing a minute quantity of dry hydrogen chloride in solution has little or no action on metallic sodium ; it is suggested that the reason why ethylic malonate dried by silicon tetrachloride does not react with sodium (Nef, Abstr., 1892, 140) is the presence of small quantities of hydrogen chloride.

Sodium does not react with methylic dimethylacetoacetate at the ordinary temperature, but at 95—100° the metal slowly dissolves, and at 115—125° the reaction proceeds vigorously and hydrogen is evolved.

When methylic dimethylacetoacetate (86 grams) is heated in a reflux apparatus at 110—120° with metallic sodium (6·9 grams), and the heating continued for 2 hours, then neutralised with acid and precipitated with water, and the ethereal layer fractionally distilled, the portion distilling below 100° consists chiefly of methylic isobutyrate. About 30 grams passes over at 220—240°, and the greater portion of this consists of *ethylic-γ-acetyldimethylacetoacetate*,

$$CH_2Ac\cdot CO\cdot CMe_2\cdot COOCH_3,$$

boiling at 228—232° ; it is a yellowish oil, miscible with alcohol, ether, or benzene in all proportions, and gives an intense red coloration with ferric chloride. Its *sodium* derivative, $CHNaAc\cdot CO\cdot CMe_2\cdot COOMe$, is obtained as a white, crystalline deposit when the ethereal salt is shaken with a solution of sodium methoxide in ether and methylic alcohol. The *copper* derivative, obtained by shaking a solution of the methylic salt in light petroleum with a solution of copper acetate, forms a pale blue, crystalline precipitate melting at 109°. The *monoxime*, obtained by heating a methyl alcoholic solution of the methylic salt with water, sodium carbonate, and sufficient hydroxylamine hydrochloride to yield the dioxime, crystallises from methylic alcohol in colourless crystals melting at 115°. No dioxime could be obtained, a fact which appears to indicate that the methylic salt contains but one carbonyl group. When the ethereal salt is heated at 120° for several hours with dilute hydrochloric acid, it is decomposed into carbonic anhydride, methylic alcohol, and *acetylisobutyrylmethane*, $CH_2Ac\cdot CO\cdot CHMe_2$, which boils at 160—170°, and yields a *copper* derivative crystallising from its hot methyl alcoholic solution in glistening, blue needles melting at 171°. Barium hydroxide induces a similar hydrolysis. When

10 grams of methylic γ-acetyldimethylacetoacetate or methylic α-dimethyltriacetate (Collie) is mixed with 25 c.c. of concentrated ammonia, and the mixture kept first in a closed vessel for several hours and then heated on the water bath, about 6 grams of *trimethyldiketotetrahydropyridine*, $CO<\begin{matrix} CMe_2\cdot CO \\ CH:CMe \end{matrix}>NH$, or *trimethyl-$\alpha$-hydroxy-$\gamma$-ketodihydropyridine*, $CO<\begin{matrix} CMe_2\cdot C(OH) \\ CH{=\!=}CMe \end{matrix}>N$, is obtained; this crystallises from hot ethylic acetate or benzene in well-developed prisms melting at 140°, but is readily soluble in hot water or in alcohol, but only sparingly in ether. When treated with an excess of phenylhydrazine, it yields a *monophenylhydrazone* melting at 155°. J. J. S.

Action of Ammonia on Ethylic Methylglyoximecarboxylate. By KARL ERBSTEIN (*Arch. Pharm.*, 1898, **236**, 150—152).—By the action of ammonia on ethylic methylglyoximecarboxylate, the amide of methylglyoximecarboxylic acid, $NOH\colon CMe\cdot C(NOH)\cdot CO\cdot NH_2$, and varying amounts of other compounds are formed according to the conditions of the experiment. In one case, a neutral substance, $C_3H_6N_2O_2$, was obtained, which decomposed at 181°, crystallised from hot water, and when heated with strong sodium hydroxide solution evolved ammonia and formed an acid melting at 135—140°. This acid the author regards as a stereoisomeride of oximidopropionic acid. When 1 part of ethylic methylglyoximecarboxylate is heated with 8 parts of concentrated ammonia at 100°, the amide of methylglyoximecarboxylic acid, the amide of methylfurazancarboxylic acid, $O<\begin{matrix} N\colon CMe \\ | \\ N\colon C\cdot CO\cdot NH_2 \end{matrix}$, methylglyoxime, oximidomethyloxazolone, and a volatile acid with an odour like acetic acid are formed. The amide of methylglyoximecarboxylic acid crystallises from hot water in colourless prisms, or plates, sinters at 180°, and decomposes and intumesces at 183°; it is easily soluble in alcohol, acetone, and hot water, sparingly so in ether, chloroform, and benzene, and dissolves in cold sodium hydroxide solution with liberation of ammonia; with ferric chloride in aqueous solution, it gives a yellowish-red coloration, and by the action of warm hydrochloric acid it decomposes into oxalic acid and oximidomethyloxazolone. By the action of boiling sodium hydroxide solution, oximidopropionic acid (m. p. 177°), and methyloximido-oxazolone are formed, and when heated with ammonia it yields the amide of methylfurazancarboxylic acid; the latter crystallises in lustrous needles, melts at 124°, and is easily soluble in alcohol, chloroform, and hot water; when boiled for a short time with sodium hydroxide solution, it yields ammonia and Wolff's methylfurazancarboxylic acid, $C_4H_4N_2O_3 + H_2O$, whilst by the prolonged action of the alkali, oximidopropionic acid is obtained. E. W. W.

Malic Acid from Crassulaceæ. By J. H. ABERSON (*Ber.*, 1898, **31**, 1432—1449).—The acid was prepared chiefly from *Echeveria secunda glauca* and *Sedum purpurescens* (*Bryophyllum calycinum* yields more, namely, about 0·23 per cent. of the leaves, but is less easily

obtainable) by extraction with boiling water, precipitation of the lead salt, and decomposition of this with hydrogen sulphide. The residue left on evaporation of the aqueous solution, when dried at 110° until constant in weight, has the composition $C_8H_8O_8$; it represents an anhydride of the acid, for the salts prepared from it are derived from a dibasic acid, $C_4H_6O_5$. The *calcium hydrogen* salt is usually amorphous, but was once obtained in regular octahedra with $6H_2O$; the corresponding salt of ordinary malic acid crystallises in rhombic octahedra. The *barium* salt is anhydrous, whereas ordinary barium malate crystallises with $1H_2O$. The *silver* salt is anhydrous, whereas ordinary silver malate contains $5H_2O$. The *lead* salt crystallises with $3H_2O$. No ammonium hydrogen salt could be prepared, whereas ordinary malic acid forms a well crystallised salt of this composition. The *dimethylic* salt was prepared from the anhydride and methylic alcohol by Anschütz's method; it distils at 162° under 25 mm. pressure; after this has passed over, a second product is obtained, to which reference will be made later. The dimethylic salt is converted by alcoholic ammonia at 100° into the *amide*, which melts at 174—178°. The formula assigned to the acid above was confirmed by determinations of the freezing point of aqueous solutions, and of the electrical conductivity of the sodium salt. The acid has the specific rotation $[\alpha]_D = +9{\cdot}8°$ at 15° in aqueous solution, that of ordinary malic acid being $-5{\cdot}8°$; the anhydride has $[\alpha]_D = -39{\cdot}5°$ in acetone solution, and it is found that concentrated solutions of the acid in water are increasingly lævorotatory, doubtless owing to the formation of anhydride. The potassium and sodium salts are lævorotatory. When the acid is distilled under diminished pressure, a little fumaric acid and some maleic anhydride distil over, but the bulk passes over as the anhydride of the acid itself; a little carbonic anhydride and oxide, and some aldehyde, are formed in addition. Much the same thing happens under ordinary pressure, except that a large part of the acid remains behind in the flask. When ordinary malic acid is distilled under diminished pressure, fumaric acid and maleic anhydride are formed in almost theoretical amount; no gas is evolved. It has been said that the acid from *Crassulaceæ*, unlike ordinary malic acid from mountain-ash berries, forms an anhydride. This anhydride is itself a dibasic acid, and has probably the constitution

$$COOH{\cdot}CH{<}^{O\cdot CO\cdot CH_2}_{CH_2\cdot CO\cdot O}{>}CH{\cdot}COOH;$$

it may be called *malide*. Its *dimethylic* salt, boiling at 210° under about 25 mm. pressure, and melting at 102°, distils over finally in the preparation of the dimethylic salt mentioned above; its *diethylic* salt, boiling at 245—250° under 30 mm. pressure, is the sole product of the action of ethylic alcohol on the anhydride. Boiling with potash converts the malide into the malic acid; heating with water for a short time only carries this change to the half-way stage, the product yielding a silver salt, $C_8H_7O_9Ag_3$. This same silver salt is obtained by the action of aqueous silver nitrate on the malide; alcoholic silver nitrate, mixed with the calculated quantity of alcoholic ammonia, forms the true silver salt of the malide, $C_8H_6O_8Ag_2$. The diethylic

salt is completely converted into the malic acid when boiled for 10 hours with water. The analogy between this malic acid and *d*-lactic acid is striking.

This malic acid is reduced to succinic acid by hydriodic acid and phosphorus at 100°; further, it is a dibasic acid, and, being optically active, it must contain an asymmetric carbon atom, so that its formula must be $COOH\cdot CH_2\cdot CH(OH)\cdot COOH$. There are three possible configurations of this formula, which may be assumed to possess a certain degree of stability:

$$\text{I.}\ \begin{array}{r@{}c@{}l} & \text{OH} & \\ & | & \\ \text{H}\cdot & \text{C} & \cdot\text{COOH} \\ & | & \\ \text{COOH}\cdot & \text{C} & \cdot\text{H} \\ & | & \\ & \text{H} & \end{array} \qquad \text{II.}\ \begin{array}{r@{}c@{}l} & \text{OH} & \\ & | & \\ \text{H}\cdot & \text{C} & \cdot\text{COOH} \\ & | & \\ \text{H}\cdot & \text{C} & \cdot\text{COOH} \\ & | & \\ & \text{H} & \end{array} \qquad \text{III.}\ \begin{array}{r@{}c@{}l} & \text{OH} & \\ & | & \\ \text{H}\cdot & \text{C} & \cdot\text{COOH} \\ & | & \\ \text{H}\cdot & \text{C} & \cdot\text{H} \\ & | & \\ & \text{COOH} & \end{array}$$

Of these, I represents ordinary malic acid, which is mostly converted into fumaric acid when distilled, and II may be regarded as an unstable form momentarily assumed by a part of this acid before its conversion into maleic anhydride. The acid from the *Crassulaceæ* must have the configuration III, which must therefore be regarded as no less stable than I, contrary to Wislicenus' views, according to which I, being the more "favoured" configuration, ought to be the only stable one. C. F. B.

Reciprocal Transformation of Tartaric, Racemic, and Mesotartaric Acids. By ARNOLD FREDERICK HOLLEMAN (*Rec. Trav. Chim.*, 1898, **17**, 66—85).—The difference in micro-crystalline character of the calcium salts of the three acids renders it possible to detect a trace of any one of them in presence of the other two. For quantitative separation the following process gives good results: the aqueous solution of the free acids is evaporated on the water-bath, until crystallisation commences, and then left during 24 hours; the racemic acid separates quantitatively, and is carefully drained and weighed. The mother liquor is diluted to a suitable volume (20 c.c.), and half of the latter exactly neutralised by caustic potash; on adding the unneutralised portion and leaving overnight, a quantitative separation of potassium hydrogen tartrate is obtained, which is washed with very little water, and weighed. By neutralising the filtrate with ammonia, slightly acidifying with acetic acid, boiling and adding calcium chloride, the mesotartaric acid is completely precipitated, and, after 24 hours, can be collected and weighed as calcium salt.

Employing this method, the author has studied the behaviour of pure tartaric, racemic, and mesotartaric acids (in each case 6 grams being taken), when heated with 4 c.c. of normal hydrochloric acid in sealed tubes at fixed temperatures between 109° and 155°.

From tartaric acid, at temperatures below 140°, mesotartaric acid is almost the sole product, traces only of racemic acid being formed; after heating 42 hours at 155°, however, the amount of the latter is 6·7 per cent., that of the former being 18 per cent.; considerable decomposition, however, occurs between 140° and 155°, which is shown by the great increase in pressure in the tubes.

Whilst 19 per cent. of mesotartaric acid is formed on heating racemic acid with normal hydrochloric acid during 100 hours at 140°, 10 per cent. only of racemic acid is obtained from mesotartaric acid under the same conditions; these facts explain the preponderance of mesotartaric acid in the product obtained from tartaric acid at 140°.

Meissner has stated (Abstr., 1897, i, 460) that small quantities only of mesotartaric acid are formed on treating tartaric acid for 8 hours with boiling alkali; the author finds, however, that under these circumstances 24 per cent. of the former acid is obtained, the yield being a maximum (31·5 per cent.) after two hours heating; so that this affords a method of preparing mesotartaric acid much more rapid than that proposed by Jungfleisch.

In discussing the theoretical side of the question, the author points out that, since di-isobutylic tartrate is not changed when heated for 72 hours at 200°, the reciprocal transformation of the acids dealt with depends solely on the hydrogen ions. The fact that mesotartaric acid is formed with greater ease than racemic acid from tartaric acid, is explained by assuming that, whereas the production of the former involves only one of the asymmetric carbon atoms, that of the latter is dependent on both of them being changed. W. A. D.

Conversion of Gluconic Acid into *d*-Arabinose. By Otto Ruff (*Ber.*, 1898, **31**, 1573—1577. Compare Cross, Bevan and Smith, Trans., 1898, 463).—Calcium gluconate was oxidised in two ways: with bromine in the presence of lead carbonate and water at the ordinary temperature, when the oxidation is complete in 10 hours if the mixture is shaken frequently; and also with hydrogen peroxide (containing 1·2 per cent. of oxygen) and a little basic ferric acetate solution at 38°, the mixture being allowed to stand for 3 days and the excess of peroxide then removed by treatment with freshly precipitated manganese dioxide. In both cases, about two-thirds of an atom of oxygen was used per 1 mol. of the gluconate; the product was treated with alcoholic hydroxylamine, and d-*arabinoseoxime* was obtained eventually; this melts at 138—139°, and shows multirotation, reaching finally the value $[\alpha]_D = -13·23°$ at 20° in 8 per cent. aqueous solution; when heated with phenylhydrazine and acetic acid, it yields an *osazone* melting at 159—160° when crystallised from water, and at 162—163° when first crystallised from benzene; with parabromophenylhydrazine it yields a *bromosazone* melting at 163°.

Calcium gluconate (1 mol.) can be oxidised simply by basic ferric acetate (1 mol.) in sunlight; the products are arabinose and a little formaldehyde. C. F. B.

Action of Hydriodic Acid on Aromatic Bromine Derivatives. By Josef Herzig (*Monatsh.*, 1898, **19**, 90—94).—When dibromodiethylorcinol or tribromodihydroxybenzoic acid (m. p. 187—189°) is heated with hydriodic acid of sp. gr. = 1·7, the bromine is completely removed, showing that when two hydroxyl groups are present in the meta-position, the third group can be methyl or carboxyl without the nature of the reaction suffering any change.

With tribromometahydroxybenzoic acid and hydriodic acid, the reaction is slower, the whole of the halogen not being removed until after

heating for 18 hours, instead of from 2 to 3 hours as in the previous cases. The conclusion might be drawn that this reaction depends only on the symmetrical position of the three bromine atoms, the presence of two or three substituents in the meta-position being only of secondary importance; this argument, however, does not appear to hold good, for symmetrical tribromobenzoic acid was heated for 30 hours with hydriodic acid without suffering decomposition.

Orthobromotoluene, and ortho- and para-bromobenzoic acids are not affected by boiling with hydriodic acid.

The author has already shown (Abstr., 1886, 232) that brominated phloroglucinol derivatives give up their bromine when treated with dilute alkalis, and it seemed possible that this and the action of hydriodic acid might be corresponding reactions. Experiment, however, does not support this belief, for tribromodihydroxybenzoic acid does not give up bromine on treatment with dilute alkalis. A. W. C.

Coloured Compounds obtained from Sodium Alkyloxides and Picryl Chloride. By CHARLES LORING JACKSON and W. F. BOOS (*Amer. Chem. J.*, 1898, **20**, 444—455. Compare Abstr., 1897, i, 332). —The exact constitution of the compounds produced in this reaction is still unknown. Empirically they consist of a molecule of an alkyl picrate combined with 1 molecule of sodium alkyloxide. The authors point out that the experimental results are opposed to the constitution suggested by V. Meyer (Abstr., 1895, i, 95) in which one hydrogen atom of the benzene nucleus is represented as being replaced by sodium. The *methylic* compound, $C_6H_2(NO_2)_3 \cdot OMe,MeONa$, produced by the action of excess of sodium methoxide on picryl chloride in methylic alcohol, separates in the form of scarlet needles, decomposes at 165°, and explodes violently when heated to higher temperatures. Water or methylic alcohol slowly decomposes it, and acids cause immediate decomposition, trinitranisoil being produced in both cases. According to Meyer's hypothesis, its formula would be

$$C_6HNa(NO_2)_3 \cdot OMe,MeOH,$$

and it should therefore contain methylic alcohol of crystallisation, but the substance suffers no loss in weight when heated at 130°, and it has not been found possible to obtain the compound $CHNa(NO_2)_3 \cdot OMe$.

On crystallising the methylic compound from ethylic alcohol, the *ethylic* compound, $C_6H_2(NO_2)_3 \cdot OEt,EtONa$, is produced; this closely resembles the former but yields ethylic picrate on treatment with acids.

The *propylic* compound, $C_6H_2(NO_2)_3 \cdot OPr,PrONa$, resembles the methylic compound, and is similarly prepared. On treatment with acids, *propylic picrate*, $C_6H_2(NO_2)_3 \cdot OPr$, is obtained, which crystallises in almost colourless needles and melts at 43°.

The *isoamylic* compound, $C_6H_2(NO_2)_3 \cdot OC_5H_{11},C_5H_{11}ONa$, forms an amorphous, orange precipitate, and when treated with acids yields isoamylic alcohol and *isoamylic picrate*; the latter crystallises in almost colourless, hexagonal plates which melt at 68—69°. The *benzylic* compound, $C_6H_2(NO_2)_3 \cdot OC_7H_7,C_7H_7 \cdot ONa$, forms red needles and exhibits fluorescence. *Benzylic picrate*, $C_6H_2(NO_2)_3 \cdot O \cdot CH_2Ph$, is sparingly soluble in alcohol and crystallises in nearly colourless plates which melt at 115°.

When picryl chloride, or trinitranisoil, dissolved in methylic alcohol, is treated with an aqueous solution of barium hydroxide, a *compound* separates in red crystals apparently of the formula

$$[C_6H_2(NO_2)_3\cdot OMe]_2, BaH_2O_2 + 10H_2O;$$

when dried at 110—130°, it loses water and its composition then approximates to that indicated by the formula $[C_6H_2(NO_2)_3OMe]_2, BaH_2O_2$. The anhydrous compound is dark crimson, but on exposure to air it absorbs water and regains the scarlet colour of the hydrated substance; acids decompose it, yielding trinitranisoil. Calcium hydroxide gives rise to a similar compound, which is more unstable. G. T. M.

Bromoveratrole. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1897, [iii], 17, 114).—The bromoveratrole which Gaspari (Abstr., 1897, i, 30) obtained by the action of bromine on veratrole in acetic acid solution, appears to be identical with the product prepared by the author by diazotising veratrylamine in presence of hydrobromic acid and finely divided copper (Abstr., 1896, i, 426). Both are represented by the formula $C_6H_3Br(OMe)_2$ [Br : OMe : OMe = 1 : 3 : 4]. N. L.

Action of Iodine on the Lead Derivative of Catechol. By CHARLES LORING JACKSON and WALDEMAR KOCH (*Ber.*, 1898, 31, 1457—1460).—If quinol is dissolved in water, neutralised with the calculated quantity of potassium hydroxide, and then treated with the calculated quantity of lead acetate, a lead derivative is obtained; when a concentrated alcoholic solution of iodine is added to this, lead iodide is precipitated, and ordinary quinone can be extracted from the aqueous solution.

When the same operations are gone through with catechol instead of quinol, a red chloroform extract is obtained, but no crystalline substance can be isolated from it. This solution contains no catechol; it must be assumed to contain orthobenzoquinone, for when it is shaken with ammonium sulphide solution, sulphur is deposited and catechol is formed; when gaseous hydrogen chloride is passed into it, monochlorocatechol is formed; and when it is boiled with an excess of aniline a dianilidoquinoneanil, $O{:}C_6H_2(NHPh)_2{:}NPh$ [O : NPh : $(NHPh)_2$ = 1 : 4 : 2 : 5], melting at 203°, is formed, identical with that obtained from the paraquinone. C. F. B.

The Oxidation of Aniline. By EUGEN BAMBERGER and FRED TSCHIRNER (*Ber.*, 1898, 31, 1522—1528).—When aniline is oxidised with free hypochlorous acid (not bleaching powder), in addition to azobenzene, &c., small quantities of paramidophenol, benzoquinonechlorimide, $O{:}C_6H_4{:}NCl$, and paramidodiphenylamine are formed. The paramidophenol was undoubtedly formed by the molecular transformation of phenylhydroxylamine, and the paramidodiphenylamine by the action of the last substance on aniline; it was not possible to detect phenylhydroxylamine amongst the products of oxidation of aniline, it is true, but nitrosobenzene, a substance into which it is converted very easily, can be obtained in considerable amount by oxidising aniline in sulphuric acid solution with potassium permanganate, in the presence of a little formaldehyde. The various stages in the oxidation of aniline can now be represented by the following schedule :—

$$C_6H_5\cdot NH_2 \rightarrow C_6H_5\cdot NH\cdot OH \rightarrow C_6H_5\cdot NO \rightarrow C_6H_5\cdot NO_2$$
$$C_6H_5\cdot NO \rightarrow C_6H_5\cdot N{:}N\cdot C_6H_5$$
$$C_6H_5\cdot NH\cdot OH \rightarrow OH\cdot C_6H_4\cdot NH_2 \rightarrow O{:}C_6H_4{:}O$$
$$C_6H_5\cdot NH\cdot OH \rightarrow C_6H_5\cdot NH\cdot C_6H_4\cdot NH_2 \rightarrow C_6H_5\cdot N{:}C_6H_4{:}NH$$

C. F. B.

Action of Nitric Acid on Tribromacetanilide. By WILLIAM B. BENTLEY (*Amer. Chem. J.*, 1898, 20, 472—481).—The author has endeavoured to prepare the tribromonitraniline melting at 214—215° which Remmers (this Journal, 1874, 696) described as being obtained by acetylating symmetrical tribromaniline, nitrating the anilide, and hydrolysing the resulting nitro-compound with aqueous or alcoholic ammonia in sealed tubes at 180—200°. Körner's preparation obtained from metanitraniline melted at 102·5°, and is, therefore, not identical with Remmers'.

The author easily obtained tribromacetanilide, but was unable to prepare tribromonitracetanilide, for fuming nitric acid acted on tribromacetanilide at the ordinary temperature, but only yielded oily products mixed with unaltered anilide. Tetrabromobenzene was the only product which could be recognised when the tribromo-compound was boiled with concentrated nitric acid. On heating the anilide with 80 per cent. acetic acid and nitric acid (sp. gr. 1·4), bromanil, dibromodinitromethane, and oxalic acid were formed. As a means of characterising the bromanil, the author endeavoured to prepare the dibromodiphenoxyquinone described by Jackson and Grindley, but on treating bromanil with sodium phenoxide in absolute alcohol, *dibromodiethoxyquinone* is obtained; it crystallises from alcohol in orange-red prisms, and melts at 139°. Since this substance can also be obtained from bromanil made by Stenhouse's method, there can be no doubt as to the identity of the compound obtained in the author's experiments with the latter. Jackson and Grindley's dibromodiphenoxyquinone is obtained by using 95 per cent. alcohol in the above reaction. G. T. M.

Reactions of Organic Ammonium Salts—Correction. By JULIUS TAFEL (*Ber.*, 1898, 31, 1349).—The benzene ring in phenyltrimethyl ammonium bromide (this vol., i, 471) is not acted on by chlorine or bromine, but the salt itself, like all quaternary ammonium salts, combines with bromine to form a *perbromide*, NMe_3PhBr_3, which crystallises from warm alcohol in yellowish-red needles melting at about 112°. When its acetone solution is gently warmed, it yields the colourless phenyltrimethylammonium bromide. J. J. S.

Isomeric Phenyltolylmethenylamidines. By O. ZWINGENBERGER and REINHOLD WALTHER (*J. pr. Chem.*, 1898, [ii], 57, 209—231).—Diphenylmethenylamidine, $NPh{:}CH\cdot NHPh$, was prepared by adding a mixture of aniline and formanilide to excess of phosphorus trichloride; the product is identical with that prepared from aniline and ethylic orthoformate; the *picrate* and *platinochloride* melt at 187° and 228° respectively. Those of diparatolylmethenylamidine (prepared from paratoluidine and ethylic orthoformate) both melt at 211°.

One *phenylparatolylmethenylamidine*, presumably with the constitution $NPh{:}CH\cdot NH\cdot C_6H_4Me$, is obtained from aniline, formoparatolu-

idide, and phosphorus trichloride; it melts at 98°, its *picrate* and *platinochloride* at 196° and 207°. A *second*, presumably with the same constitution, is obtained by heating diphenylmethenylamidine with paratoluidine at 100°; it melts at 120°, its *picrate* and *platinochloride* at 178° and 213°. Yet a *third*, presumably with the constitution $C_6H_4Me\cdot N:CH\cdot NHPh$, is obtained from paratoluidine, formanilide, and phosphorus trichloride; it melts at 102°, its *picrate* and *platinochloride* at 193° and 218°. And a *fourth*, presumably with the same constitution as the last, is obtained by heating diparatolylmethenylamidine with aniline hydrochloride in alcoholic solution; it melts at 132°, its *picrate* and *platinochloride* at 209° and 127°. These substances are all different; although the melting point 98° seems near to 102°, the first of the substances in question is twice as soluble in light petroleum as the second. When boiled in light petroleum solution for 5 hours, the compound melting at 98° is converted into that melting at 102°. An attempt to prepare a fifth isomeride, $NPh:CH\cdot NMePh$, failed; no stable product is obtained when diphenylmethenylamidine is heated with methylic (or ethylic) iodide. Neither will this amidine yield an acetic or benzoic derivative; acetanilide and benzanilide were obtained instead. Cold fuming nitric acid oxidises it to paranitraniline. It will not react with phenylcarbimide; it does, however, react with hydroxylamine hydrochloride and with phenylhydrazine when heated with these substances, the products being *phenylmethenylamidoxime*, $NOH:CH\cdot NHPh$, melting at 128—129°, and *diphenylmethenylhydrazidine*, $NHPh\cdot N:CH\cdot NHPh$, melting at 90—91°.

A *phenylorthotolylmethenylamidine*, $NPh:CH\cdot NH\cdot C_6H_4Me$, is obtained from formorthotoluidide, aniline, and phosphorus trichloride, and melts at 100°, its *picrate* and *platinochloride* at 168—169° and 206—207°. An identical substance is obtained, although the yield is not good, by heating aniline with diorthotolylmethenylamidine; the picrate and platinochloride are also identical with the above. The same substance is yet again obtained by heating diphenylmethenylamidine with orthotoluidine. A *second* isomeride,

$$C_6H_4Me\cdot N:CH\cdot NHPh,$$

is, however, obtained from orthotoluidine, formanilide, and phosphorus trichloride; it melts at 109—110°, its *picrate* and *platinochloride* at 176° and 209—210° respectively. The compound melting at 100° can be partially converted into that melting at 110° by boiling it in light petroleum solution; before the conversion is complete, however, decomposition sets in.

The substances described in the paper were crystallised from light petroleum, as a rule. The picrates and platinochlorides were yellow.

C. F. B.

Reaction of Phenylhydroxylamine with Alcoholic Sulphuric Acid and with Aniline. By Eugen Bamberger and Jan Lagutt (*Ber.*, 1898, 31, 1500—1508).—The authors, like Haber (*Zeit. Elektrochem.*, No. 22), have also studied the action of alcoholic sulphuric acid on phenylhydroxylamine. When 100 grams of phenylhydroxylamine were digested with 2400 c.c. of commercial absolute alcohol and 50 c.c.

of sulphuric acid (sp. gr. 1·84) for 26 hours on the water bath (in two lots), the weights (in grams) of the following products obtained were :—Azoxybenzene, 14 ; paraphenetidine, 46 ; orthophenetidine, 8 ; paramidophenol, 3·5 ; orthamidophenol, 3·5 ; aniline, 4 ; dark fluorescent oil, 2 ; nitrobenzene, phenol, and a base resembling a semidine (probably paramidodiphenylamine), traces ; colouring matters, not determined. The formation of orthamidophenol (and orthophenetidine) is noteworthy, for, under the influence of aqueous sulphuric acid, only paramidophenol has hitherto been obtained. How the phenetidines are formed is not quite clear ; they cannot be formed from the amidophenols, for these give no ethylic derivatives when heated with alcoholic sulphuric acid ; nor can they be formed by an intramolecular transformation of the ethylic derivative of phenylhydroxylamine, for this substance does not yield such a derivative when heated with alcoholic sulphuric or hydrochloric acid (neither does *benzyl*hydroxylamine).

When 75 grams of phenylhydroxylamine dissolved in 100 grams of freshly-distilled, dry aniline is added gradually to a mixture of 105 grams aniline hydrochloride with 130 grams aniline already heated to 130°, rinsed in with 15 grams of aniline and the whole then maintained at that temperature for 40 minutes, there are obtained :—Azoxy- (and azo-) benzene, 17—18 ; colouring matters, 18—19 ; benzidine sulphate, 10 ; paramidodiphenylamine sulphate, 8·6 ; orthamidodiphenylamine and a little diphenyline (?), 6·4 ; aniline, not estimated ; bases of the paramidodiphenylamine type (anilides of amidodiphenylamines ?) and chloraniline, traces.

From the final mother liquor, obtained after nitrosophenylhydroxylamine has been allowed to decompose spontaneously in benzene solution, and the products already described (this vol., i, 366) have been separated, a very small quantity of diphenyl can be obtained by evaporating the benzene, and reducing the residue with stannous chloride and boiling hydrochloric acid. C. F. B.

Reaction of the Nitrosoalphyls with Concentrated Sulphuric Acid. By Eugen Bamberger, Hans Büsdorf, and H. Sand (*Ber.*, 1898, 31, 1513—1522).—Nitrosoalphyls react very readily with concentrated sulphuric acid at 0°, and a yellow product is precipitated on diluting with water ; the reaction is of the nature of an aldol condensation ; from nitrosobenzene, for example, *nitrosodiphenylhydroxylamine*, $OH\cdot NPh\cdot C_6H_4\cdot NO$, is formed. This substance decomposes at 147—152°, and has acid properties ; it is reduced by zinc dust and water to paramidodiphenylamine, and by sulphurous acid to a new *paramidodiphenylaminesulphonic acid*, which yields paramidodiphenylamine when it is distilled with ammonium chloride ; it forms a dark yellow *monacetyl* derivative, melting between 146° and 157° ; when treated with nitric oxide, it yields diazodiphenylamine nitrate, which unites with β-naphthol to form a brownish-black *azo-dye* melting at 164—165° and identical with the product prepared by diazotising paramidodiphenylamine and uniting the product with β-naphthol.

4-*Nitroso-2′ : 3-ditolylhydroxylamine*, $C_6H_4Me\cdot N(OH)\cdot C_6H_3Me\cdot NO + H_2O$, from orthonitrosotoluene, decomposes at about 130° ; the yellow

monobenzoyl derivative melts and decomposes at 181—182°; when reduced, it yields 4-*amido*-2′:3-*ditolylamine*, which melts at 63—64°, is very unstable in the air, and yields a *monacetyl* derivative melting at 122·5°, and a yellow *salicylidene* derivative melting at 112°. 2′:3-*Dibromo*-4-*nitrosodiphenylhydroxylamine*, from *orthobromonitrosobenzene* (which melts at 97·5—98°), melts and decomposes between 118° and 123°, its *monacetyl* derivative at 144—145°; when reduced, it yields 2′:3-*dibromo*-4-*amidodiphenylamine*, which melts at 70°, and froths up when heated in a test-tube, leaving a residue from which alcohol extracts a blue colouring-matter.

When paranitrosotoluene is treated with strong sulphuric acid, one bromine atom is lost and 4′-*bromo*-4-*nitrosodiphenylhydroxylamine* is formed; this decomposes at 154°.

The salicylidene derivatives of amidodiphenylamines are decomposed by phenylhydrazines; with phenylhydrazine, salicylideneparamidodiphenylamine yields colourless (not yellow) salicylic phenylhydrazone and amidodiphenylamine; with paranitrophenylhydrazine, orange-red *salicylic paranitrophenylhydrazone*, melting at 223°, is formed. From salicylideneparamidoditolylamine and phenylhydrazine, salicylic phenylhydrazone and paramidoditolylamine are formed. C. F. B.

The Decomposition of Diazo-compounds. By E. C. Franklin (*Amer. Chem. J.*, 1898, **20**, 455—466).—The author gives a detailed account of the method he employs in preparing ortho- and metamidobenzenesulphonic acids. The three amidobenzenesulphonic acids differ somewhat in their susceptibility to the action of nitrous acid. The ortho-acid, suspended in a finely divided condition in ethylic alcohol, is easily diazotised when subjected to the action of nitrous fumes, whilst with the para-acid when thus treated the action is never complete, and the meta-acid cannot be satisfactorily diazotised in alcohol, although when suspended in water the reaction proceeds quite readily.

The decomposition of the para- and meta-diazobenzenesulphonic acids by methylic and ethylic alcohols has been previously studied by Shober and Kiefer (Abstr., 1893, i, 639; and 1895, i, 520), and the author now furnishes the results obtained in the case of the third isomeride.

Orthodiazobenzenesulphonic acid, when decomposed by methylic alcohol, yields only orthomethoxybenzenesulphonic acid, which is identified by means of its chloride and amide; the methoxy-compound is the sole product whether the action be carried out under atmospheric pressure or under greater or less pressures. Similarly, orthoethoxybenzenesulphonic acid is the only product of the action of ethylic alcohol. This behaviour of the ortho-acid is contrasted with that of its two isomerides; thus in the case of the meta-compound substitution of hydrogen occurs, especially at the lower pressures and when the higher alcohol is employed, whilst the para-compound yields chiefly benzenesulphonic acid, except when methylic alcohol acts on it under increased pressure; in this case, methoxybenzenesulphonic acid predominates.

When paramethoxybenzenesulphonamide is added to well-cooled

fuming nitric acid and the liquid is diluted with water, a small quantity of metadinitrobenzene is obtained; the filtrate after removing the nitric acid by evaporation with alcohol and neutralising with potash, yields the *potassium* salt of a mononitroparamethoxybenzenesulphonic acid; its *sulphonamide* forms yellow needles and melts at 138—140°.

A considerable amount of metadinitrobenzene is obtained on nitrating paraethoxybenzenesulphonamide. Orthomethoxybenzenesulphonamide, on nitration, yields a small quantity of metadinitrobenzene, but this compound is not obtained on nitrating the metasulphonamide. G. T. M.

Azammonium Compounds. By RUDOLF NIETZKI and ALFRED RAILLARD (*Ber.*, 1898, 31, 1460—1464).—When dinitrodiphenylmethylamine, $NMePh\cdot C_6H_3(NO_2)_2$ [$N:(NO_2)_2 = 1:2:4$] (Leymann, Abstr., 1882, 1057), is dissolved in acetic acid, treated with fuming nitric acid, and allowed to remain, *tetranitrodiphenylmethylamine*, presumably $NMe[C_6H_3(NO_2)_2]_2$ [$NMe:(NO_2)_2 = 1:2:4 = 1':2':4'$], is formed; this is yellow and melts at 210°.

When it is suspended in aqueous-alcoholic ammonia, and hydrogen sulphide is passed in, no considerable rise of temperature being allowed to take place, *amidodinitrodiphenylmethylamine*,

$$NO_2\cdot C_6H_3(NH_2)\cdot NMe\cdot C_6H_3(NO_2)_2 \ [NH_2 = 2],$$

melting at 190°, is formed. When this is boiled with excess of acetic anhydride, it yields an anhydro-base,

$$NO_2\cdot C_6H_3 \begin{array}{l} \diagup NMe(OH)\cdot C_6H_3(NO_2)_2 \\ \diagdown N:CMe \end{array},$$

which is yellow, and melts at 264°.

When treated with nitrous acid, it yields trinitrodiphenylmethylazammonium hydroxide, $NO_2\cdot C_6H_3 \begin{array}{l} \diagup NMe(OH)\cdot C_6H_3(NO_2)_2 \\ \diagdown N:N \end{array}$; this is yellow, has no determinate melting point, and no basic properties; it can be reduced by ammonium sulphide to an orange-red *amido*-compound, $NO_2\cdot C_6H_3 \begin{array}{l} \diagup NMe(OH) \\ \diagdown N:N \quad NH_2 \end{array} > C_6H_3\cdot NO_2$ [$NH_2 = 2'$], and when this is treated with nitrous acid a yellow product is obtained which does not melt without decomposing, and probably has the constitution

$$NO_2\cdot C_6H_3 < \overline{N:N} > NMe < \overline{O\cdot N:N} > C_6H_3\cdot NO_2.$$

If, in the reduction of tetranitrodiphenylmethylamine with ammonium sulphide, the temperature is allowed to rise to the boiling point of the solution, *diamidodinitrodiphenylmethylamine*,

$$NMe[C_6H_3(NH_2)\cdot NO_2]_2 \ [(NH_2)_2 = 2:2']$$

is formed; nitrous acid converts it into the substance mentioned at the end of the last paragraph. C. F. B.

Ketone Musks. By ALBERT BAUR-THURGAU (*Ber.*, 1898, 31, 1344—1349).—When the ketone obtained by introducing a benzoyl group into butyltoluene is nitrated, no compound of musk-like odour is obtained; if, however, an acetyl group is introduced into butyltoluene

or butylxylene and the methyl ketones thus obtained are nitrated, products are obtained which have a strong odour of musk.

Butyltoluene (1 part), carbon bisulphide (10 parts) and aluminium chloride (6 parts) are cooled in a flask, and acetic chloride (6 parts) run in as quickly as possible; after distillation on the water bath, the residue is poured on to ice and treated in the usual manner. The *acetyl* derivative is obtained as an oil with a pleasant aromatic odour boiling at 255—258°. When nitrated at 0° with 100 per cent. nitric acid, a *dinitro*-derivative, $C_{13}H_{16}N_2O_5$, is obtained; it crystallises in broad needles, melts at 131°, and has a strong odour of musk. The acetyl group in this compound does not occupy the symmetrical position, but takes the place of one of the nitro-groups in butyltrinitrotoluene. When 1 : 3 : 5-butylxylene is oxidised by boiling for 3 days with dilute nitric acid, *butyltoluic acid* is obtained; this is readily soluble in dilute alcohol, sparingly in light petroleum, and crystallises in colourless plates melting at 162°. The *acid chloride* is a liquid boiling at 258—260°, and when treated with sodium ethylic acetoacetate, and the product thus obtained hydrolysed, a solid *ketone*, $C_{13}H_{18}O$, melting at 47° and boiling at 260°, is obtained; it yields a dinitro-derivative melting at 103° which has no musk-like odour.

Butylxylyl methyl ketone, $C_{14}H_{20}O$, obtained by slowly adding acetic chloride (50 grams) to butylxylene (100 grams) and aluminium chloride (30 grams) and treating in the usual manner, crystallises from ether in large plates melting at 48° and boiling at 265°, and is readily soluble in alcohol, benzene, and light petroleum. It does not react with hydroxylamine, nor yet with phenylhydrazine, and when treated at 0° with 100 per cent. nitric acid yields a *dinitro*-derivative, $C_{14}H_{18}N_2O_5$, melting at 136° and having an odour of musk. This nitro-derivative does not yield an oxime or a phenylhydrazone, but yields a *benzylidene* derivative melting at 140° and a *trichlorethylidene* derivative melting at 179°.

When oxidised with alkaline permanganate below 65°, butylxylyl methyl ketone yields *butylxylylglyoxylic acid*, which cannot be crystallised and which melts, by no means sharply, at 90—110°. Its *methylic* salt is an oil, but yields a *dinitro*-derivative, $C_{15}H_{18}N_2O_7$, melting at 127°. The glyoxylic acid, when heated with Nordhausen sulphuric acid, yields *butylxylylcarboxylic acid* melting at 168°, and readily soluble in alcohol or benzene, but when heated with aniline or paratoluidine according to Bouveault's method, *butylxylylaldehyde* is obtained. When reduced, the glyoxylic acid is converted into *dimethylbutylmandelic acid*, $C_4H_9\cdot C_6H_2Me_2\cdot CH(OH)\cdot COOH$, which crystallises in colourless plates melting at 120°. When the ketone is oxidised with alkaline permanganate at temperatures above 70°, the products are butylxylylcarboxylic acid, the glyoxyl- carboxylic acid, and the -dicarboxylic acid. The filtrate from the manganese dioxide is acidified, and the oily mixture of acids is added in small portions at a time to boiling 40—50 per cent. sulphuric acid to which an equal weight of zinc dust is slowly added. When cold, the mixture is filtered and the residue extracted with sodium carbonate, and the acid obtained by acidifying the alkaline solution is heated in an oil bath to 200°; the fused mass then consists of butylxylylcarboxylic acid, *butylmethylphthalide* and *butyl-*

phthalidecarboxylic acid; the phthalide, which remains behind when the mixture is extracted with sodium carbonate solution, has a slight smell of benzaldehyde, is readily soluble in the usual solvents with the exception of water, and when nitrated with 100 per cent. nitric acid yields two isomeric *mononitro*-derivatives; the one melts at 154° and is readily soluble in alcohol, and the other melts at 181° and is more sparingly soluble. Butylxylylcarboxylic acid (m. p. 168°) is obtained from the mixture of the two acids by extraction with 50 per cent. alcohol; the phthalidecarboxylic acid crystallises from absolute alcohol in colourless needles melting at 273°.

When the ketone is oxidised with dilute nitric acid, the chief product is Hollemann's dinitrosacyl (Abstr., 1888, 275), which, when warmed with sodium hydroxide solution, yields butylxylylcarboxylic acid. When the oxidising agent employed is 60 per cent. nitric acid, the product is *dinitrodinitrosacyl*, $(C_{14}H_{16}N_2O_4)_2$, which crystallises from alcohol in needles melting at 176°, and when warmed with sodium hydroxide yields *nitrobutylxylylcarboxylic acid*, melting at 190°. *Tetranitrodinitrosacyl*, formed when 100 per cent. nitric acid is used, crystallises from chloroform in thick prisms, melts at 245°, and is insoluble in alcohol or light petroleum; when warmed with alkali, it yields *dinitrobutylxylylcarboxylic acid* melting at 236°. The *methylic* salt of this acid is obtained when the *acid chloride*, which crystallises from benzene in needles melting at 99°, is treated with sodium methoxide; it crystallises from alcohol in pale yellow needles melting at 96°.

When ketone musk is oxidised with potassium permanganate under exactly the same conditions as were employed for the ketone, the product is a dinitroglyoxylic acid, which could not be obtained in a crystalline form, and the methylic salt of which has been previously described. When oxidised in acetic acid solution with either permanganate or chromic anhydride, the product is the dinitro-acid melting at 236°.

Butylxylyl butyl ketone, $C_{16}H_{24}O$, melts at 50° and distils at 290—295° its *dinitro*-derivative melts at 128° and smells like musk. *Butylxylyl amyl ketone* is an aromatic oil distilling at 185—190° under 14 mm. pressure; its *dinitro*-derivative crystallises from alcohol in long, yellow needles melting at 151°, and has a strong odour of musk. J. J. S.

Nitration of Methylic Benzoate. By H. J. Taverne (*Rec. Trav. Chim.*, 1898, **17**, 96—99).—On nitration, methylic benzoate gives rise to products similar to those obtained from benzoic acid; the methyl group is therefore without influence. Methylic metanitrobenzoate is the principal product of the action at 0°; a small proportion, however, of *methylic orthonitrobenzoate* is formed; this is a slightly yellow liquid which boils at 183° under a pressure of 22 mm., has a sp. gr. = 1·2855 at 20°, and, when solidified, melts at −13°. It is best prepared by adding silver benzoate to well-cooled methylic iodide; it is also formed on passing hydrogen chloride into a solution of benzoic acid in methylic alcohol, or by heating the latter solution with sulphuric acid; in both cases, however, the yield is poor.

W. A. D.

Separation of Ortho- and Meta-nitrobenzoic Acids. By H. J. Taverne (*Rec. Trav. Chim.*, 1898, **17**, 100—101).—When hydrogen chloride is passed through a solution of ortho- and meta-nitrobenzoic acids in methylic alcohol, the meta-acid is converted completely into its methylic salt, whilst only a small proportion of the ortho-salt is produced; crystals of methylic metanitrobenzoate separate on cooling, whilst the ortho-salt, being a liquid, remains dissolved. After purification, the meta-methylic salt is easily hydrolysed by baryta water.

W. A. D.

Some Properties of Aromatic Orthohydroxy-compounds. By Isidor Traube (*Ber.*, 1898, **31**, 1566—1571).—The molecular volume in solution of sodium salicylate is different from that of sodium para- or meta-hydroxybenzoate, and agrees well with that calculated on the assumption that the acid has some such constitution as $CH{<}\begin{matrix}CH_2\cdot CO\\CH\cdot CH\end{matrix}{>}COOH$; no such difference is to be observed between sodium ortho- and meta-hydroxy*hexahydro*benzoates. In accordance with this view is the fact that salicylic acid, unlike its two isomerides, develops practically no heat when mixed with a second molecule of soda; other physical properties also afford confirmatory evidence. Further, salicylic acid in different solvents gives, with ferric chloride, a series of colours very similar to those given by ethylic acetoacetate (probably it is not hydroxy-compounds that alone give colorations with ferric chloride, but mainly aromatic keto-compounds that give red or violet colorations; compare Morrell and Crofts, Trans., 1898, 345). Salicylic acid would appear not to be a mixture of two isomerides, for the specific gravity of an alcoholic solution of ethylic salicylate does not alter with the time.

Again, catechol has a smaller volume in solution than resorcinol or quinol, and, unlike the last two, it gives out little heat when mixed with a second molecule of soda. Probably it is a mixture of two isomerides, *k* and *e*, which give respectively a deep red and a green coloration with ferric chloride.

C. F. B.

Phenylglutaric Acid and its Derivatives. By Samuel Avery and Rosa Bouton (*Amer. Chem. J.*, 1898, **20**, 509—515).—The authors find that benzylidene chloride and ethylic sodiomalonate do not give rise to ethylic benzylidenedimalonate, but to ethylic benzylidene malonate. The latter substance, when treated with ethylic sodiomalonate in alcoholic solution, and subsequently acidified with dilute sulphuric acid, yields an oil which appears to consist chiefly of ethylic benzylidenedimalonate. On boiling this oil with strong hydrobromic acid for 24 hours, evaporating the product to dryness, extracting the residue with hot water, and crystallising from dilute hydrochloric acid, β-phenylglutaric acid is obtained; it forms glistening plates soluble in water, alcohol, ether and chloroform, and benzene, insoluble in light petroleum, and melts at 140°. It is identical with the acid obtained by Michael by the action of ethylic sodiomalonate on an alkylic cinnamate. The *barium, copper, lead,* and *akali* salts are described.

β-Phenylglutaric anhydride, produced when the acid is heated above its melting point, or when treated with acetic chloride, forms glisten-

ing, white plates and melts at 105°; it is soluble in benzene, chloroform, and ether, insoluble in light petroleum. *β-Phenylglutaranilic acid*, formed from aniline and the anhydride, melts at 168°. *β-Phenylglutaranil*, obtained on heating the preceding compound, forms glistening, white needles melting at 223°. *β-Phenylglutaroparatolilic acid* melts at 154—155°.

When fuming sulphuric acid acts on β-phenylglutaric anhydride, a crystalline *acid* melting at 153° is produced; its *silver* salt has the composition $C_{22}H_{18}O_6Ag_2$. G. T. M.

β-Phenyl-α-methylglutaric Acid. By SAMUEL AVERY and MARY L. FOSSLER (*Amer. Chem. J.*, 1898, **20**, 516—518).—The product of the condensation of ethylic sodiomalonate with methylic α-methylcinnamate when hydrolysed, and subsequently distilled, yields an oil which is probably the impure anhydride of the above acid. The copper salt, formed on adding copper sulphate to the anhydride dissolved in ammonia, is decomposed by hydrogen sulphide, and the free β-phenyl-α-methylglutaric acid is obtained on concentrating the solution. It forms flaky, white plates, melts at 122°, and is soluble in alcohol, ether, chloroform, and hot benzene, insoluble in light petroleum. G. T. M.

Action of Phthalic Anhydride on Para- and on Meta-hydroxydiphenylamine. By ARNALDO PIUTTI and R. PICCOLI (*Ber.*, 1898, **31**, 1327—1333. Compare Abstr., 1884, 448).—When molecular quantities of phthalic anhydride and parahydroxydiphenylamine are heated together on a sand-bath, the mixture begins to melt at 60°, water is given off at 150°, and the mass solidifies and melts again at 150—195°; after keeping at this temperature for some time, the mass is pounded and extracted with sodium carbonate solution, and this extract, when acidified, yields *parahydroxydiphenylphthalamic acid*, $OH\cdot C_6H_4\cdot NPh\cdot CO\cdot C_6H_4\cdot COOH$. It crystallises from dilute alcohol in somewhat yellowish prisms melting at 191—192°, and is insoluble in water, but readily dissolves in alcohol, ether, or acetic acid. With concentrated sulphuric acid, it yields a blue coloration, which disappears on the addition of alcohol or water. When heated above its melting point, the acid yields an *anhydride*. The *silver* salt, $C_{20}H_{14}NO_4Ag + 3\frac{1}{2}H_2O$, and *copper* salt, $(C_{20}H_{14}NO_4)_2Cu + 4H_2O$, are both described. The *ethylic* salt crystallises in needles melting at 166—168°. *Paramethoxydiphenylphthalamic acid*, obtained by treating an alcoholic solution of the hydroxy-acid with potassium hydroxide and methylic iodide, can best be purified by dissolution in alcohol and fractional precipitation with water; it is insoluble in water, but dissolves readily in alcohol, ether, or acetone, and melts at 90—92°; the corresponding *ethoxy*-derivative melts at 80—82°. Sparingly soluble *acetyl* and *benzoyl* derivatives have been obtained, and they, together with the above-mentioned compounds, yield the characteristic coloration with sulphuric acid.

The residue left after extraction with sodium carbonate consists of a coloured substance which is insoluble in the usual solvents but dissolves in sulphuric acid; the addition of water to this solution precipitates a strongly coloured resin. The same coloured product is

obtained when an excess of parahydroxydiphenylamine reacts with phthalic anhydride.

Molecular quantities of the anhydride and metahydroxydiphenylamine react in pretty much the same manner; the mixture is completely fused at 120°, and at a higher temperature becomes solid again; when purified by crystallisation from alcohol, *metahydroxydiphenylphthalamic acid* is obtained in the form of yellowish crusts, which turn violet at 185° and melt at 191—192°; the *sodium*, *potassium*, *ammonium*, and *silver* salts have been prepared. When heated at its melting point, the acid loses water, and is converted into the corresponding rhodamine; dehydrating agents yield the same product. The *ethylic* salt melts at 155—157°, the *methoxy*-derivative melts at 95—98° and becomes coloured at 120°, and the *ethoxy*-derivative melts at 90°.

The *rhodamine*, $C_{32}H_{22}N_2O_3$, is obtained when phthalic anhydride (1 mol.) is heated with metahydroxydiphenylamine (2 mols.) at about 150—160° for 2 hours, and can best be purified by repeated extraction with alcohol; it is sparingly soluble in ether, more readily in benzene or carbon bisulphide, yielding colourless solutions. Its *hydrochloride* forms small, violet crystals, and when its alcoholic solution is treated with bromine, the violet colour is partially destroyed.

In a single instance the mother liquors from the rhodamine yielded a crystalline compound melting at 207°, and possessing the properties of phenylphthalimide.

J. J. S.

Action of Ethylic Oxalate on Paramidophenol and its Ethers. By ARNALDO PIUTTI and R. PICCOLI (*Arch. Pharm.*, 1898, **236**, 153—160, and *Gazzetta*, **28**, i, 284—298).—See this vol., i, 319.

E. W. W.

Aromatic Sulphamic Acids—Correction. By CARL PAAL (*Ber.*, 1898, **31**, 1327). In reply to Junghahn (this vol., i, 479), the author states that free sulphamic acids, namely, paratolyl- and α-naphthyl-sulphamic acids, were prepared some two years ago by Jänicke Lowitsch and himself (Abstr., 1896, i, 235; 1897, i, 351).

J. J. S.

Action of Oxides of Nitrogen on Mercury Alphyls. By JAKOB KUNZ (*Ber.*, 1898, **31**, 1528—1531. Compare Bamberger, Abstr., 1897, i, 288).—When mercury paraditolyl, $(C_6H_4Me)_2Hg$, is mixed with nitrogen trioxide at 0—15°, the product is mercuryparatolyl nitrate, $C_6H_4Me\cdot Hg\cdot NO_3$, together with paratolyldiazonium nitrate and a little paranitrosotoluene. With nitrogen tetroxide under similar circumstances, it gives mercuryparatolyl nitrate and paranitrosobenzene. With nitric oxide, no reaction takes place in the absence of air; when air is admitted, the same products are obtained as with nitrogen trioxide. Mercuryorthoditolyl behaves in the same way as the para-compound.

Mercury-α-dinaphthyl yields, with nitrogen trioxide, mercury-α-naphthyl nitrate and α-naphthyldiazonium nitrate, but no nitrosonaphthalene. With nitrogen tetroxide, it yields mercury-α-naphthyl nitrate and some naphthalene, but neither α-naphthyldiazonium nitrate nor nitrosonaphthalene.

C. F. B.

Tetrahydropyrone Compounds. By PAVEL IW. PETRENKO-KRITSCHENKO (*Ber.*, 1898, 31, 1508—1512).—When a mixture of acetonedicarboxylic acid (1 mol.) and methylsalicylaldehyde (2 mols.) with an equal volume of acetic acid and some hydrochloric acid is allowed to remain overnight, *dimethoxydiphenyltetrahydropyronedicarboxylic acid*, $CO<\begin{matrix}CH(COOH)\cdot CH(C_6H_4\cdot OMe)\\CH(COOH)\cdot CH(C_6H_4\cdot OMe)\end{matrix}>O$, is formed. When heated on the water bath, this loses carbonic anhydride and yields *dimethoxydiphenyltetrahydropyrone*, $CO<\begin{matrix}CH_2\cdot CH(C_6H_4\cdot OMe)\\CH_2\cdot CH(C_6H_4\cdot OMe)\end{matrix}>O$, which melts at 173°. Boiling with acetic anhydride does not convert this into an unsaturated ketone, but heating it in alcoholic solution with a few drops of hydrochloric acid for $\frac{1}{4}$ hour on the water bath does effect this conversion: *dimethoxydibenzylideneacetone*,

$$CO(CH\dot{:}CH\cdot C_6H_4\cdot OMe)_2,$$

is yellow and melts at 123°; its *tetrabromide* is colourless and melts at 174°.

When the substituting group in the phenyl residues is not neutral in character, like methoxyl, but acid, no condensation to a pyrone takes place. Acetonedicarboxylic acid and paranitrobenzaldehyde yield an *acid*, $CO[CH(COOH)\cdot CH(OH)\cdot C_6H_4\cdot NO_2]_2$, which loses carbonic anhydride when heated on the water bath, forming yellow *diparanitrobenzylideneacetone*, $CO(CH\dot{:}CH\cdot C_6H_4\cdot NO_2)_2$; this melts at 254°, its colourless *tetrabromide* at 239°; it may also be obtained by adding a few drops of aqueous soda to a mixture of paranitrobenzaldehyde with acetone.

Metanitrobenzaldehyde and metachlorobenzaldehyde condense with acetonedicarboxylic acid forming *ketones*, which melt at 239° and 123° respectively. C. F. B.

Reaction of Benzaldehyde with Phenol. By ARTHUR MICHAEL (*J. pr. Chem.*, 1898, [ii], 334—336).—Benzaldehyde may condense with phenol to dihydroxytriphenylmethane in the presence of a moderate quantity of a mineral acid (Russanoff, Abstr., 1889, 188), but in the presence of traces only of acid the product is hydroxybenzhydrol, as the author showed previously, for when it is distilled with zinc dust and the distillate is fractionated under diminished pressure diphenylmethane is obtained. The first stage in the interaction between an aldehyde and a phenol undoubtedly consists in an aldol condensation; whether a further condensation takes place between this first product and a second molecule of the phenol depends on the nature of the latter and on the amount of mineral acid present.

C. F. B.

Cedrirets. By RUDOLF NIETZKI and R. BERNARD (*Ber.*, 1898, 31, 1334—1338. Compare Nietzki, Abstr., 1878, 868).—The ditolylcedriret, $(C_7H_5OMe)_2O_2$, previously obtained by the oxidation of toluquinol methylic ether, when heated with an alcoholic solution of hydroxylamine hydrochloride, yields a *monoxime*, $C_{16}H_{17}NO_4$, crystallising in bronzy, glistening needles, and only sparingly soluble in the usual solvents; it dissolves in alkalis, may be recrystallised from amylic alcohol, and yields a *monacetyl* derivative. When this oxime

is warmed with about six times its weight of nitric acid (sp. gr. 1·3) and the solution allowed to cool, a *nitro*-derivative, $C_{14}H_{11}NO_5$, is obtained, which crystallises from alcohol in beautiful, red needles; when heated with acetic anhydride, the nitro-compound yields an *acetyl* derivative, crystallising in pale yellow needles and melting at 143°. Brunner's ditolyldiquinone (Abstr., 1889, 996) may be obtained by oxidising ditolylcedriret with dilute nitric acid, or by the oxidation of dimethyltoluquinol with chromic acid mixture. The following constitutions agree best with the reactions and methods of preparation of the different compounds.

Nitro-derivative, $NO_2\cdot C_6H_2Me(OH)\cdot C_6H_2MeO_2$, $NO_2 : Me : OH = 2:3:5$ and $Me : O_2 = 3' : 2' : 5'$; monoxime,

$$C_6H_2Me(OMe)_2\cdot C_6H_2MeO\colon NOH,\quad Me : (OMe)_2 = 3 : 2 : 5$$

and $O : Me : NOH = 2' : 3' : 5'$; ditolylcedriret,

$$C_6H_2(OMe)_3\cdot C_6H_2MeO_2,\quad (OMe)_3 = 2 : 3 : 5$$

and $O : Me : O = 2' : 3' : 5'$. J. J. S.

Nitrogen Compounds of the Menthol Series and their Derivatives. By MICHAËL KONOWALOFF and W. TSCHEWSKY (*Ber.*, 1898, 31, 1478—1481).—When menthone is nitrated with nitric acid of sp. gr. 1·075, in an open vessel, at 80°, with constant stirring, a nitromenthone, probably $C_3H_7\cdot C(NO_2){<}{\scriptstyle CO-CH_2 \atop \scriptstyle CH_2\cdot CH_2}{>}CHMe$, is formed (Abstr., 1896, i, 177); it has a rotation greater than +39°, although the menthone employed was *lævo*rotatory. The crude nitromenthone was reduced with tin and hydrochloric acid to *amidomenthone*, $NH_2\cdot C_{10}H_{17}O$, which boils at about 125° under 25 mm., at 235—237° under ordinary pressure, has sp. gr. = 0·9750 at 0°/0°, 0·9606 at 20°/0°, and index of refraction $n_D = 1·47397$ at 20°, and is fairly soluble in water. The *hydrochloride* melts and decomposes at 245—247°; no other salts could be made to crystallise. Amidomenthone forms an *oxime* which boils at 182—185° under 20 mm. pressure, the *hydrochloride* of which melts at 110°; also a *semicarbazone* melting at 80°, and a crystalline *benzoyl* derivative. Amidomenthone in alcoholic solution is reduced by sodium to *mentholamine* (*amidomenthole*), $NH_2\cdot C_{10}H_{17}\cdot OH$, a viscous liquid boiling at 147—150° under 20 mm., and at 254° under ordinary pressure; its specific rotation $[\alpha]_D = -6°$; it is fairly soluble in water. Its *sulphate* melts at 250°; no other salt could be prepared.

Amidomenthonoxime in alcoholic solution is reduced by sodium to a *diamine*, $C_{10}H_{18}(NH_2)_2$, which boils at 240—243°; the salts crystallise badly, but the platinochloride and the mercurochloride were obtained crystallised; the hydrochloride reacts vigorously with potassium nitrite, yielding a liquid which boils at 220°, and is apparently an unsaturated ketone, identical or isomeric with pulegone. C. F. B.

Guaiacum Resin. II. By JOSEF HERZIG and F. SCHIFF (*Monatsh.*, 1898, 19, 95—105. Compare Abstr., 1897, i, 165, 254, and this vol., i, 327).—Pyroguaiacin crystallises from alcohol in beautiful, glistening leaflets melting at 180—183°, and on analysis gives numbers agreeing with the formula $C_{13}H_{14}O_2$. When treated with acetic anhydride and sodium acetate, it yields *acetylpyroguaiacin*, $OAc\cdot C_{13}H_{13}O$, crystallising

from alcohol in flat, glistening needles melting at 122—124° (compare Weiser, *Monatsh.*, 1880, 1, 594).

Attempts to arrive at the nature of guaiaretic acid have so far proved fruitless, for when the acetyl derivative is oxidised with chromic acid in acetic acid solution no crystalline substance could be obtained. The acid gives a *diethyl* derivative crystallising from alcohol in flat, white needles or leaflets, melting at 100—102° and distilling in a vacuum without decomposition. A. W. C.

Lichens and their Characteristic Constituents. By OSWALD HESSE (*J. pr. Chem.*, 1898, [ii], 57, 232—318. Compare Abstr., 1895, 298).—This long paper contains an account of the constituents of a number of lichens, these constituents being described under the heading of the lichens from which they were obtained respectively. The methods by which they were obtained are described in detail, but it may be said that the method generally adopted was to extract a portion of the lichen, usually in coarse fragments, with 100—200 c.c. of ether in a reflux apparatus until nothing more was dissolved; the ether was as free from alcohol as possible, in some cases entirely so. If no appreciable deposit had formed during 10 hours in the ethereal extract, the latter was used for the extraction of a fresh portion of the lichen. Had a deposit formed, it was filtered off, and the ethereal solution concentrated so as to obtain a fresh quantity of the deposit. Often the ethereal solution was shaken with aqueous potassium hydrogen carbonate; this removed acids (except usnic acid), which were afterwards set free with hydrochloric acid and extracted with ether. Sometimes the filtered ethereal extract was evaporated to dryness; if small quantities of usnic acid were present, this acid was dissolved out by boiling with a mixture of 9 parts of light petroleum and 1 of benzene; or in other cases, the solid residue was treated with a limited quantity of alcohol, the hot solution being filtered from the undissolved part and diluted with water until a turbidity just appeared; or some other of the recognised methods of organic chemistry was employed. Below is a list of the lichens examined, with the localities in which they were found, and the substances obtained from them; where melting points and formulæ differ from those previously assigned by the author or others, the present ones may be assumed to be more correct, the material employed having been purer.

Usnea longissima Acharius, from Garmisch (near Stuttgart?) and Rauhmünzach in the Black Forest.—Usnic acid; the conversion of this substance into decarbusnein is effected particularly easily by heating it with four times its weight of acetone for 4 hours at 150°. [This acid is identical with the old α-usnic acid; the prefix is no longer necessary, as "β-usnic acid" has been shown to be a mixture of usnic acid itself with atranorin]. *Barbatic acid*, $C_{22}H_{24}O_8$ (Stenhouse and Groves, $C_{19}H_{20}O_7$), is monobasic; the *potassium* and *barium* salts, with $1\frac{1}{2}$ and $3H_2O$ respectively, and the green *copper* salt were prepared and analysed. The *ethylic* salt, obtained by heating the potassium salt with ethylic iodide at 150°, melts at 132°; in alcoholic solution, it gives a bluish-violet coloration with ferric chloride.

U. barbata (L.) Fries, from Traunstein, Bavaria.—Usnic and barbatic acids.

U. barbata f. *dasypoga* (Ach.) Fr. and f. *hirta* (L.) Fr., from Java cinchona bark.—Usnic acid. *Usnaric acid*, $C_{30}H_{22}O_{15}$, is but little soluble in ether, except when just liberated from a salt; it crystallises in aggregates of needles, decomposes at 240—260° without melting, has a very bitter taste, and gives a purplish-violet to brownish-red coloration with ferric chloride; it is possibly identical with Zopf's salaz(in)ic acid (this vol., i, 90). *Usnarin* crystallises in prisms and melts and decomposes at 180°; it is insoluble in cold alkalis, and has no taste.

U. ceratina (Ach.).—Usnic acid, barbatic acid, and barbatin.

Evernia vulpina (Ach.), from the Engadine, and also from California, where it occurs on the *Wellingtonia*, and is known as "moss of the big trees."—Vulpic acid and atranorin.

E. divaricata (L.) Ach., from Schörzingen (?).—*Divaricatic acid*, $C_{21}H_{23}O_6\cdot OMe$, is crystalline, melts at 129°, and gives a purplish-violet coloration with ferric chloride in alcoholic solution; a *barium* salt, $C_{22}H_{24}O_7Ba + 2H_2O$, was prepared and analysed, and in the mother liquor from it another salt, probably of an acid $C_{11}H_{14}O_4$, was found.

E. prunastri (L.) Ach.; var. *vulgaris*, Körber, from near Stuttgart, and var. *gracilis* from Liebenzell, Black Forest.—Evernic acid, usnic acid, and atranorin.

E. furfuracea (L.) Ach., from Feuerbach, near Stuttgart.—Atranorin only.

Ramalina pollinaria (Westr.) Ach., from Feuerbach.—Usnic acid. Atranorin. Evernic acid, $C_{16}H_{13}O_6\cdot OMe$: the *potassium* salt, $C_{17}H_{15}O_7K + 2H_2O$, was prepared; when this is heated with ethylic iodide and alcohol, it does not form an ethylic salt, but yields ethylic everninate, orcinol, and carbonic anhydride, according to the equation $C_{17}H_{15}O_7K + EtI + H_2O = C_9H_9O_3\cdot OEt + C_7H_8O_2 + CO_2 + KI$; the acid forms insoluble basic barium and calcium salts; it is decomposed by boiling with baryta water into orcinol and *barium everninate*, $C_9H_8O_4Ba + H_2O$ or $(C_9H_9O_4)_2Ba + 8H_2O$, as the case may be; orcinol is also obtained when the acid is heated with hydriodic acid. Ramalic acid, $C_{16}H_{13}O_6\cdot OMe$: the anhydrous *potassium* and sparingly soluble *barium* salts were prepared; the acid gives a purplish-violet coloration with ferric chloride; boiled with baryta, it yields the same products as evernic acid does, and no doubt the isomerism between these two acids consists in the different way in which the lactone-condensation has taken place.

Ramalina ceruchis (Ach.), from a speciman of Californian "orseille."—Usnic acid. An acid melting at 135°, fairly soluble in cold alcohol; and another, less soluble, decomposing at 220—260° (usnaric acid ?).

Roccella Montagnei Bél., from Ceylon, Zanzibar, Madagascar, and Angola.—Erythrin: probably

$$C_4H_6(OH)_3\cdot O\cdot CO\cdot C_6H_2Me(OH)\cdot O\cdot CO\cdot C_6H_2Me(OH)_2,$$

a condensation product of erythritol with lecanoric acid; crystallises from dilute acetic acid with $1H_2O$ and melts when anhydrous at 148° (not 137°). *Oxyroccellic acid*, $C_{15}H_{30}O(COOH)_2$: melts at 128°; gives

no coloration with ferric chloride or bleaching-powder solution; the anhydrous *barium* and *silver* salts were prepared and analysed; when heated at 160—180°, the acid yields the *anhydride* which melts at 82°; when heated with acetic anhydride at 85°, it yields an *anhydride*, $O(CO \cdot C_{15}H_{30}O \cdot COOH)_2$, which melts at 121°.

R. fuciformis (L.) D.C.—Erythrin and oxyroccellic acid.

R. peruensis Krempelhuber [syn. *R. cacticola*, Darbishire, and *R. fruticosa* (*frutectosa*) Laurer], from California.—Erythrin. Oxyroccellic acid. Roccellic acid, $C_{17}H_{32}O_4$, a dibasic acid; the *barium*, with $1\frac{1}{2}H_2O$, *calcium*, *copper*, and *silver* hydrogen-salts and the normal *lead* salt were prepared and analysed.

R. tinctoria (L.) Ach., from Cape Verde.—Oxyroccellic, roccellic and parellic acids. Lecanoric acid, $C_{16}H_{14}O_7 + H_2O$, a monobasic acid; gives in alcoholic solution, like erythrin, a blood-red coloration with bleaching-powder solution; the *potassium*, *barium*, *calcium*, *copper*, and *basic lead* salts, with 1, 5, 4, 2 and 0 H_2O respectively, were prepared and analysed; when heated with acetic acid, the acid first yields orsellinic acid, but this readily loses carbonic anhydride, forming orcinol; heated with methylic alcohol at 85°, it yields carbonic anhydride, orcinol, and methylic orsellinate, which melts at 138°, and has a great resemblance to methylic betorcinolcarboxylate. Orsellinic acid crystallises from dilute acetic acid with $1H_2O$, from alcohol with 2 (and 1) H_2O.

R. portentosa Mtg., from Chili.—Lecanoric acid only.

R. canariensis Darbishire, from Teneriffe.—Lecanoric acid only.

R. sinensis Nylander, from Tonquin.—Lecanoric acid.

R. decipiens Darbishire. An acid, sparingly soluble in ether, melting at 142°, and giving a brownish coloration with ferric chloride.

R. intricata (Mtg.) Darbishire. Zeorin. *Roccellaric acid*; crystalline, melts at 110°, gives a bluish-violet coloration with ferric chloride, but none with bleaching-powder solution.

Reinkella birellina Darbishire, from Lima, Peru. Roccellic or oxyroccellic acid. Roccellinin.

Darbishirella gracillima (Krph.) Zahlbruckner (syn. *Roccella intricata* Mtg.), from Chili.—Parellic acid.

Dendrographa leucophæa (Tuck.) Darbishire, from San Diego, Mexico. Protocetraric acid. Further, a crystalline substance which melts at 121°, and gives a brownish-red coloration with ferric chloride.

Cladonia rangiferina (L.) Hoffmann, from Feuerbach.—Usnic acid.

C. pyxidata (L.) Fries, from Feuerbach.—Parellic acid.

C. coccifera (L.) Schaerer, from Brand in the Vorarlberg.—Coccellic acid.

C. rangiformis, Hoffmann, from Stockheim on Keuper sandstone ("Schilfsandstein"), and from Feuerbach on Keuper marl ("Mergel"); the first sample gave twice as large a yield as the second.—Atranorin, rangiformic acid, and atranorinic acid; further, a wax which melts at 81° and has the composition $C_{28}H_{54}O_2$. Rangiformic acid, $C_{20}H_{33}O_5 \cdot OMe$, sometimes crystallises with $2H_2O$; it is a dibasic acid; the *potassium*, *barium*, *calcium*, *copper*, *lead*, and *silver* salts, with 0, 2, $1\frac{1}{2}$, $1\frac{1}{2}$, 2, and 0 H_2O were prepared and analysed. When treated with hydriodic acid, it yields *norrangiformic acid*, $C_{18}H_{31}(COOH)_3$, of which

it is the monomethylic salt; this acid crystallises with $2H_2O$, of which it loses 1 in a desiccator, and then melts at 119°. Atranorin (atranoric acid, Paternò and Oglialoro), probably

$$COOMe\cdot C_6HMe_2(OH)\cdot O\cdot CH_2\cdot O\cdot \underset{CMe\cdot C(OH)\cdot C\cdot CO}{C\text{——}CH\text{—}C\cdot O},$$

is decomposed by heating with acetic acid at 150°, the products being, beside a resin, physciol and methylic betorcinolcarboxylate, $COOMe\cdot C_6HMe_2(OH)_2$; of these, the former dissolves more rapidly in boiling water. Physciol (atranorinic acid, Paternò), probably $C_6H_2Me(OH)_3$ [1 : 2 : 4 : 6], when heated with acetic anhydride at 85°, forms an oily *monacetyl* derivative, from which a very small quantity of crystals, melting at 78°, separated; both of these substances give a purple-violet coloration with ferric chloride. When boiled with acetic anhydride and sodium acetate, it yields a product which is separated by boiling with water into an insoluble oil and crystals which melt at 80—82° and have the composition $C_{11}H_{10}O_4$. Methylic betorcinolcarboxylate (physcianin, atraric acid, ceratophyllin) yields carbonic anhydride and β-orcinol when it is heated with hydriodic acid; it greatly resembles its next lower homologue, methylic orsellinate, and, like it, gives a blood-red coloration with bleaching-powder solution. Theoretically, the hydrolysis of atranorin ought to yield, in addition to physciol and methylic betorcinolcarboxylate, formaldehyde and carbonic anhydride; it was not found possible to demonstrate the formation of formaldehyde, however. The final products of hydrolysis with baryta are methylic alcohol, physciol, β-orcinol, carbonic anhydride, and a little resin (polymerised formaldehyde?). When atranorin is heated with methylic, ethylic, or isoamylic alcohol at 150°, the products are methylic betorcinolcarboxylate and methylic, ethylic, or *isoamylic* hæmatommate, $CH_2{<}{}^{O}_{O}{>}C_6HMe(OH)\cdot COOR$ [= 4:6:1:2:3], the last of these melts at 54°, and gives a dark brown coloration with ferric chloride; the first two were named respectively hæmatomminic and hæmatommic acid by Zopf. Atranorinic acid,

$$COOH\cdot C_6HMe_2(OH)\cdot O\cdot CH_2\cdot O\cdot C{<}{}^{CH-C(OH)}_{CMe\cdot C(OH)}{>}C\cdot COOH,$$

crystallises with $1H_2O$, melts at 157° when anhydrous, gives a dark-brown coloration with ferric chloride, and is decomposed, when heated with alcohol at 150°, into physciol, β-orcinol, and carbonic anhydride.

Cetraria islandica (L.) Ach., purchased in Stuttgart and Frankfurt.—Lichenostearic acid and protocetraric acid, the second of which is dissolved out but very slowly by the ether; cetraric acid does not exist ready formed in the lichen. Lichenostearic acid, $OH\cdot C_{16}H_{26}O\cdot COOH$, melts at 120°, its *monacetic* derivative at 124°; the *barium*, sometimes with $3H_2O$, and *silver* salts were prepared and analysed. *Protocetraric acid*, $C_{30}H_{22}O_{15}$, often crystallises with $1H_2O$; it decomposes at 240—260° without melting, and although a very insoluble substance, has a very bitter taste; it gives a brownish- to claret-red coloration with ferric chloride. It contains no methoxyl group, and is hydrolysed by boiling with alcoholic potash, or with milk of lime, yielding fumaric and cetraric acids. (Usnaric acid, mentioned above, is isomeric with protocetraric acid, and behaves similarly when heated; it is perhaps

capable of hydrolysis to maleic and cetraric acids). Cetraric acid, $C_{26}H_{20}O_{12}$, has also a very bitter taste, and gives a brownish-red to purple coloration with ferric chloride; its *barium* salt was prepared and analysed.

C. juniperina (L.) Ach.—Chrysocetraric, usnic, and vulpic acids.

C. pinastri (Scop.) Ach., from Berchtesgaden, Brand in the Vorarlberg, and Baden.—Chrysocetraric, usnic, and vulpic acids; the last two differ in composition only by the elements of water. Chrysocetraric acid (perhaps $COOMe{\cdot}CPh{:}C{<}^{O}_{O}{>}C{:}CPh{\cdot}COOH$, as it resembles vulpic acid in its reactions, is yellow), and melts at 196—198° (not 178°); its yellow *potassium, barium, calcium,* and *lead* salts, with 0 or 3, 0, 4 and 2 H_2O respectively, were prepared and analysed; its yellow *ethylic* salt, from the potassium salt and alcoholic ethylic iodide at 150°, melts at 146°, its yellow monacetyl and *monobenzoyl* derivatives at 163—164° and 156°; when boiled with aqueous baryta, it yields *oxypulvic acid,* $C_{18}H_{12}O_6$. This acid is orange-red, or lighter, in colour according as it is crystallised with 2 or $1H_2O$; it melts at 207° when anhydrous; its *barium* salt, with $1H_2O$, was prepared. It is a dibasic acid, being, in fact, the acid of which chrysocetraric acid is the monomethylic salt. If boiled with acetic anhydride, it forms a yellow *anhydride* melting at 196°, and when this is boiled with methylic alcohol, the monomethylic salt (chrysocetraric acid) is first formed, and then the yellow dimethylic salt which melts at 117°; when oxypulvic acid is boiled with ethylic alcohol, a yellow *monethylic* salt, melting at 139°, homologous with chrysocetraric acid, is first formed, but is rapidly converted into the *diethylic* salt, which is also yellow and melts at 100°. Vulpic acid, $C_{18}H_{11}O_4{\cdot}OMe$, yields methylic alcohol and pulvic acid when boiled with aqueous baryta; the last acid, when heated with acetic anhydride, forms a yellow *anhydride* which melts at 214—215° (after crystallisation from benzene at 220—221°), and is converted into pulvic acid when it is boiled with acetic acid, into vulpic acid when heated with methylic alcohol. C. F. B.

Guarana Paste. By E. Kirmsse (*Arch. Pharm.*, 1898, **236**, 122—141. Compare Schaer, *ibid.*, 1890, **228**).—From guarana paste, the author has obtained the guarana tannin by extracting (1) with hot water, or (2) with alcohol at the ordinary temperature, or (3) with ether of sp. gr. = 0·750; it forms a yellowish-white, amorphous mass, with an astringent taste, is easily soluble in water, alcohol, ether containing alcohol, and in ethylic acetate, and partly soluble in absolute ether. The product obtained by the second method has a reddish tint, due to partial decomposition. By extracting the crude tannin with ether, crystals of a catechin are obtained whose properties and reactions are identical with those of the catechin of Pegu-catechin. After drying over sulphuric acid for several weeks, its analysis showed a composition corresponding with Neubauer's formula, $C_{17}H_{24}O_{10}$, and it melted at 140°; but after cooling, powdering, and drying at 150—160° it melted at 190° when again heated, intumescing and acquiring the characteristic colour of guarana. When dried at 80—90° and at 98°, the percentage of carbon increased to a mean of

62·20 and 63·08 per cent. respectively. The product obtained by extracting the paste with hot water contains the least amount of catechin. The author confirms Thoms' statement (*Pharm. Centralhalle*, 1890, 533) that the amount of caffeine in guarana has been overestimated; three samples were found to contain 2·68, 2·97, and 3·10 per cent. respectively. Cocoa, which has been stated to be an adulterant of lower qualities of guarana, was not detected in any of the samples. E. W. W.

Chemistry of Chlorophyll. By LEO MARCHLEWSKI (*J. pr. Chem.*, [ii], **57**, 330—334).—A very destructive criticism of Bode's paper (*Inaug. Diss.*, Cassel, 1898).

Action of Hydrogen Peroxide on 1-Alkylpiperidine Bases. By W. WERNICK and RICHARD WOLFFENSTEIN (*Ber.*, 1898, **31**, 1553—1561).—Merling's "hydroxymethylpiperidine,"

$$C_5H_{10}\colon N\cdot CH_2\cdot OH$$

(Abstr., 1893, i, 113), obtained by the action of hydrogen peroxide on 1-methylpiperidine, must rather be regarded as *methylpiperidine oxide*, $C_5H_{10}\colon NMe\colon O$, its hydriodide being $C_5H_{10}\colon NMeI\cdot OH$, for when it is heated at 200° with hydrochloric acid saturated at 0°, it forms 1-methylpiperidine, together with a little methylic chloride (the same reaction takes place, but with almost explosive violence, when gaseous hydrogen chloride is passed over the dry substance at 180—230°); it reacts neither with benzoic nor with benzenesulphonic chloride; it is reduced by sulphurous acid, nitrous acid, or zinc and hydrochloric acid to 1-methylpiperidine; it loses oxygen with explosive violence when submitted to dry distillation, 1-methylpiperidine being formed; and it sets free iodine from potassium iodide (although its salts do not effect this).

Ethylpiperidine oxide, $C_5H_{10}\colon NEt\colon O$, obtained by allowing 1-ethylpiperidine to remain at the ordinary temperature with the calculated quantity of 3 per cent. hydrogen peroxide solution, forms hygroscopic crystals. The yellow *picrate* melts at 142—144°; the *hydrobromide* and the *hydriodides*, with $\frac{1}{2}$HI, melting at 95°, and with 1HI, deliquescent, were prepared and analysed. In its reactions, this substance resembles the methyl analogue, except that when submitted to dry distillation it decomposes for the greater part into ethylene and δ-amidovaleraldehyde, $NH_2\cdot[CH_2]_4\cdot CHO$, although some ethylpiperidine is formed. C. F. B.

The Methylation of Indoles. By GIUSEPPE PLANCHER (*Ber.*, 1898, **31**, 1488—1499. Compare Brunner, this vol., i, 384).—When the base $C_{13}H_{17}N$, obtained by the action of ethylic iodide on 2′-methylindole (Abstr., 1897, i, 102) is oxidised with potassium permanganate, it yields an acid, $C_{13}H_{15}NO_2$, which, when it loses carbonic anhydride, is converted into the substance $C_6H_4{<}{\genfrac{}{}{0pt}{}{CEt_2}{\text{—}N}}{\geqslant}CH$, for which the name 3′ : 3′-diethylindolenine is proposed; consequently the formula of the acid must have been $C_6H_4{<}{\genfrac{}{}{0pt}{}{CEt_2}{\text{—}N}}{\geqslant}C\cdot COOH$, and

that of the original base $C_6H_4<\overset{CEt_2}{\underset{N}{—}}\gg CMe$, the base being not 4 : 4′-diethyldihydroquinoline, as has been assumed hitherto, but 2-methyl-3′ : 3′-diethylindolenine. This base is reduced by sodium to another, of which the hydrochloride melts at 217° (*loc. cit.*, p. 103); this is to be regarded as 2′-methyl-3′ : 3′-diethylindoline,

$$C_6H_4<\overset{CEt_2}{\underset{NH}{}}>CHMe,$$

not 4′ : 4′-diethyltetrahydroquinoline; from it, the first base can be regenerated by oxidation with alkaline potassium permanganate at 0°. In the same way, Ferratini's dimethyltetrahydroquinoline (Abstr., 1893, i, 603), better 2′ : 3′ : 3′-trimethylindoline, can be oxidised to 2′ : 3′ : 3′-*trimethylindolenine* (4 : 4′-dimethyldihydroquinoline), the yellow *picrate* of which melts at 158°. This base can also be prepared by heating the phenylhydrazone of methyl isopropyl ketone (which boils at 175—176° under 47 mm. pressure) with alcoholic zinc chloride on the water bath; it boils at 228—229° under 744 mm. pressure, and the *zincochloride* melts at 225°. This method of formation confirms the view that the substance is an indolenine rather than a dihydroquinoline; it might be urged that a quinoline chain is formed during the reaction by the migration of a methyl group, but this objection is met by the fact that in a case where no such migration is possible, namely, that of the phenylhydrazone of di-isopropyl ketone, a similar condensation occurs on heating with zinc chloride, a base being formed which boils at 250—260° under 750 mm. pressure, melts at 80°, and must be regarded as 3′ : 3′-*dimethyl-2′-isopropylindolenine.*

When 2′ : 3′ : 3′-trimethylindolenine, $C_6H_4<\overset{CMe_2}{\underset{N}{—}}\gg CMe$, is treated with methylic iodide, the product is the hydriodide of 1′ : 3′ : 3′-trimethyl-2′-methyleneindoline, $C_6H_4<\overset{CMe_2}{\underset{NMe}{}}>CMeI$, from which the free base, $C_6H_4<\overset{CMe_2}{\underset{NMe}{}}>C{:}CH_2$ (trimethyldihydroquinoline, E. Fischer and Steche, Abstr., 1888, 298) can be set free with potash. The same base is obtained by condensing the methylphenylhydrazone of methyl isopropyl ketone (which boils at 130—140° under 40 mm. pressure) by means of zinc chloride. In a similar fashion, the hydriodide of 1′ : 3′ : 3′-trimethyl-2′-isopropylideneindoline (pentamethyldihydroquinoline: Zatti and Ferratini, Abstr., 1892, 615) is obtained from 2′-isopropyl-3′ : 3′-dimethylindolenine and methylic iodide; it melts at 185° (not 173°), the aurochloride at about 150°, and the picrate at 148°.

C. F. B.

Ketochlorides and Orthodiketones of Azimidobenzene. By THEODOR ZINCKE (*J. pr. Chem.*, 1898, [ii], 57, 319—329).—This paper discusses the results of experimental work previously published. It has been already shown (Abstr., 1896, i, 499, 501) that the carbon ring of quinoline reacts in many cases just like one of the two rings in naphthalene; it is now shown that the same is true of the carbon ring in azimidobenzene, except that it is not possible to convert the six-atom into a five-atom carbon ring.

C. F. B.

Cycloamidines : Pyrimidine Derivatives. By HENRY LORD WHEELER (*Amer. Chem. J.*, 1898, 20, 481—490).—The author gives the name of cycloamidines to those substances having the amidine constitution $NXR^{1}\cdot CR:NR^{11}$, but which have two of the radicles R, R^1, and R^{11} replaced by a ring structure or a bivalent group.

When R^1 and R^{11} are thus replaced, cycloamidines are formed containing two nitrogen atoms in the ring, and a preliminary account of the action of alkylic haloids on compounds of this series is given in the paper. The action of alkyl haloids on cycloamidines containing only one nitrogen atom in the ring has been extensively studied, and many cases have been found in which substitution of the hydrogen atom X does not take place. 4 : 2 : 6-Anilidophenylmethylpyrimidine, $N\Big<\begin{matrix}CMe\cdot CH\\CPh—N\end{matrix}\Big>C\cdot NHPh$, a cycloamidine containing two nitrogen atoms in the ring, behaves in a similar manner, forming stable additive products with alkylic iodides from which the original base is regenerated on treatment with dilute alkali. This cycloamidine prepared from 4 : 2 : 6-chlorophenylmethylpyrimidine and aniline, yields a *hydrobromide* melting at 250° and a *hydriodide* melting at 231°; both salts form colourless needles; the *methiodide*, $C_{18}H_{18}N_2I$, crystallises from dilute alcohol in colourless needles containing $2H_2O$; and becomes anhydrous at 130°. Dilute alkalis reconvert it into the original cycloamidine. 4 : 2 : 6-*Methylanilidophenylmethylpyrimidine*, $N\Big<\begin{matrix}CMe:CH\\CPh—N\end{matrix}\Big>C\cdot NMePh$, prepared from phenylmethylchloropyrimidine and methylaniline, crystallises in colourless prisms and melts at 113°; the *platinochloride* decomposes at 228°, the *hydriodide* melts at 198°, and the *nitrate* crystallises in colourless needles or prisms and decomposes at about 170°.

4 : 2 : 6-*Anilidophenylmethylpyrimidine ethiodide*, $C_{19}H_{20}N_2I + 2H_2O$, is crystalline, and becomes anhydrous at 130°. Dilute alkalis regenerate the original cycloamidine.

4 : 2 : 6-Ethylanilidophenylmethylpyrimidine,

$$N\Big<\begin{matrix}CMe:CH\\CPh—N\end{matrix}\Big>C\cdot NEtPh,$$

prepared like the corresponding methyl derivative, crystallises in colourless prisms soluble in alcohol but not in water, and melts at 87°; the *hydrochloride* melts at 210°, and the *platinochloride* at 218°; the *hydriodide* crystallises in prisms. Ethylic bromide is without action on anilidophenylmethylpyrimidine.

2 : 6 : 4-*Phenylmethylpyrimidonemethiodide*, produced by heating phenylmethyloxypyrimidine, $N\Big<\begin{matrix}CMe:CH\\CPh\cdot NH\end{matrix}\Big>CO$, and methylic iodide at 170°, crystallises from alcohol in colourless needles and decomposes at 230°. When treated with dilute alkali, the methiodide loses the elements of hydrogen iodide and 2-*phenyl*-1(or 3) : 6-*dimethylpyrimidone*, $C_{12}H_{12}N_2O$, is obtained, which crystallises from water in large prisms and melts at 91—92°; it is basic in character, and yields soluble salts with dilute acids. The *nitrate* forms colourless, flattened prisms and melts at 195°; the *platinochloride* crystallises in orange-red prisms and darkens at 235°.

Methylbenzamidine hydrochloride, NH:CPh·NHMe,HCl, prepared from the hydrochloride of benzimidoethylic ether and methylamine, crystallises from water in colourless needles. G. T. M.

A New Product of the Oxidation of Theobromine. By Hans Clemm (*Ber.*, 1898, **31**, 1450—1453).—When theobromine is suspended in dilute hydrochloric acid, warmed to 40—50°, and oxidised with potassium chlorate, methylalloxan is the chief product (this vol., i, 178), but a second product, melting and decomposing at 201—203°, is formed in addition; this is an *oxy*-3 : 7-*dimethyluric acid*, for it is hydrolysed by aqueous baryta to methylcarbamide and mesoxalic acid; it is soluble in alkalis, but not in acids. When heated with water for an hour at 100°, it is converted into an isomeride, *iso-oxy*-3 : 7-*dimethyluric acid*, which also melts and decomposes at 201—203°, and yields the same products when hydrolysed with baryta, but is much more soluble in water than the compound first mentioned; it forms monoclinic crystals [$a:b:c = 0.7908:1:1.2092$; $\beta = 83° 9' 20''$]. The structure of these two compounds is not quite evident. C. F. B.

Pseudotheobromine, Theobromine, Theophylline, and Paraxanthine. By Herbert Pommerehne (*Arch. Pharm.*, 1898, **236**, 105—122).—From the products of the action of methylic iodide on the silver derivative of xanthine at 130—140°, the author has isolated xanthine, theobromine, and pseudotheobromine (compare Abstr., 1897, i, 129). Pseudotheobromine, when treated with methylic iodide, yields caffeine. The author has prepared the following salts of theophylline obtained from tea-extract, and of paraxanthine. Theophylline hydrochloride, $C_7H_8N_4O_2,HCl + H_2O$, crystallises in plates, loses its water and hydrochloric acid at 100°, is more soluble in water than either the hydrochloride of theobromine or of pseudotheobromine, and forms a strongly acid solution. The aurochloride, $C_7H_8N_4O_2,HAuCl_4 + H_2O$, crystallises in lemon-yellow needles, is easily soluble in water, loses its water of crystallisation at 110°, and does not melt below 285°; the corresponding salt of pseudotheobromine melts at 270°. *Theophylline platinochloride*, $(C_7H_8N_4O_2)_2,H_2PtCl_6$, crystallises in small plates, is easily soluble in water, and does not melt below 280°; pseudotheobromine platinochloride crystallises with $4H_2O$. Paraxanthine hydrochloride, $C_7H_8N_4O_2,HCl + H_2O$, crystallises in characteristic, transparent, rhombic plates, is easily soluble in water, forming a strongly acid solution, very easily soluble in hydrochloric acid, and loses its halogen acid and water at 100°; the *aurochloride*, $C_7H_8N_4O_2,HAuCl_4 + \frac{1}{2}H_2O$, crystallises in orange-yellow needles, melts at 227—228°, is sparingly soluble in cold water, more soluble in hot, and loses its water of crystallisation at 100°; the *platinochloride*, $(C_7H_8N_4O_2)_2,H_2PtCl_6$, forms small, reddish-yellow needles, and does not melt below 290°. E. W. W.

Quinoline-morphine. By Paul Cohn (*Monatsh.*, 1898, **19**, 106—113. Compare Abstr., 1897, i, 170).—2-*Quinoline-morphine*, $C_9NH_6·O·C_{17}H_{17}NO·OH$, prepared by the action of 2-chloroquinoline on morphine, crystallises from alcohol in star-like groups of small

prisms melting at 158°. Unlike morphine, it is insoluble in alkalis, and gives no colour reaction with ferric chloride. With bromine, it yields a substitution product, and with iodine a periodide. It forms both normal and acid salts, the latter being amorphous. The normal *hydrochloride* is a hard mass crystallising with difficulty; the *platinochloride* is a pale yellow precipitate, decomposing without melting at 180—190°; the normal *sulphate* crystallises from water in slender, glistening needles, melting and giving off gas at 257°, and has a specific rotation $[\alpha]_D = -66{\cdot}46°$; the *chromate* is obtained as a yellow precipitate; the *tartrate* separates from alcohol in beautiful, transparent, glistening prisms, melting and giving off gas at 98°, whilst the *picrate* forms small, yellow crystals, melting and decomposing at 250—252°.

The normal sulphate is a strong poison, 0·001—0·002 gram producing death in cold-blooded, and 0·02 gram in warm-blooded animals. It produces clonic spasms, lessens the blood pressure, and retards the action of the pulse.

It was found impossible to replace the hydrogen atom of the second hydroxyl group in morphine by a quinoline residue. A. W. C.

Tropic Acid. III. Constitution of the Products of Decomposition of Atropine and Cocaine. By RICHARD WILLSTÄTTER (*Ber.*, 1898, 31, 1534—1553. Compare also this vol., i, 159).—When piperylenedicarboxylic acid (Abstr., 1896, i, 266) is reduced with sodium amalgam in aqueous solution at 100°, pimelic acid, $COOH\cdot[CH_2]_5\cdot COOH$, is obtained. A second product, more readily soluble in cold water, is obtained in addition; this, which is a *dihydropiperylenedicarboxylic acid*, perhaps $COOH\cdot CH{:}CH\cdot[CH_2]_3\cdot COOH$, melts at 120—121°, its *dibromide* (*dibromopimelic acid*) at 140°. When carbonic anhydride is passed through the solution during the reduction, no pimelic acid is formed, but only a *dihydropiperylenedicarboxylic acid*, isomeric with the first, however, and possibly of the constitution $COOH\cdot[CH_2]_2\cdot CH{:}CH\cdot CH_2\cdot COOH$; this acid melts at 91°, but not sharply; the *dibromide* melts at 130°. When piperylenedicarboxylic acid is heated with hydriodic acid at 170—180°, it is converted into a lactone-acid, probably the *γ-hydroxypimelic acid lactone*, $COOH\cdot[CH_2]_2\cdot CH<\overset{\text{——O——}}{CH_2\cdot CH_2}>CO$; this melts at 82·5°, and has the electrolytic dissociation constant $K = 0{\cdot}00272$ ($\mu_\infty = 376$); its silver salt is very readily soluble in water; that of the hydroxypimelic acid is less soluble, and was analysed.

The formation of normal pimelic acid by the addition of four hydrogen atoms to piperylenedicarboxylic acid makes it necessary to regard the latter as a normal acid, contrary to the view previously taken; it is probably $COOH\cdot CH{:}CH\cdot CH{:}CH\cdot CH_2\cdot COOH$, although the position of the double bonds is not certain. And as this acid is obtained from methylic *i*- or *d*-tropate (by the addition of methylic iodide and treatment with potash alternately), and the optically isomeric tropic acids are obtained by the oxidation of tropine or ecgonine (with chromic and sulphuric acids), the formulæ proposed by Merling for these alkaloids, and hitherto adopted by the author, must be given up,

and the following assigned instead (in that of ecgonine the CH·OH and CH·COOH groups may be interchanged, and in any case ecgonine is not the acid, but its betaine, or intramolecular salt).

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CH2·CH —CH2            CH2·CH—CH·OH
|    NMe CO            |    NMe CH·COOH.
CH2·CH—CH2             CH2·CH—CH2
   Tropine.                Ecgonine.
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The formulæ of a number of products of the decomposition of these alkaloids are deduced; that of tropic acid, for example, is $\begin{matrix} CH_2\text{———}CH(COOH) \\ CH_2\cdot CH(CH_2\cdot COOH) \end{matrix}\!\!>\!NMe$. It is impossible to reproduce this part of the paper in an abstract; the original must be consulted.

C. F. B.

Pilocarpidine. By C. Emanuel Merck (*Arch. Pharm.*, 1898, **236**, 141—149. Compare this vol., i, 283).—According to the author, Petit and Polonowsky's method of converting pilocarpine into pilocarpidine by heating the hydrochloride at 200° (Abstr., 1897, i, 581 and 583) does not affect the composition of the salt, although its rotatory power is diminished. When pilocarpidine hydrochloride is similarly treated, a product is obtained which has a lower rotatory power than the original hydrochloride. In aqueous solution, it yields a platinochloride melting at 184—186°, and whose content of platinum corresponds with the formula $(C_{10}H_{14}N_2O_2)_2,H_2PtCl_6$; from the mother liquor, small, apparently cubic, crystals of a platinochloride $(C_{10}H_{14}N_2O_2)_2,H_2PtCl_6 + 2H_2O$ separate. Neither by heating pilocarpine with hydrochloric acid in aqueous solution, nor by boiling it with water according to Hardy and Calmels' methods, could pilocarpidine be obtained; in each case, there was a diminution of rotatory power, but no change in composition.

E. W. W.

Hydrolysis of Proteids. By A. Eichholz (*J. Physiol.*, 1898, **23**, 163—177).—From white of egg three substances can be separated, each capable of yielding an osazone corresponding with phenylglucosazone; they are, in order of solubility, ovo-mucoid, egg-albumin, ovo-mucin. The last-named substance has not been previously described.

Pure serum-albumin yields no osazone, and the glucoproteid reaction of the mixed serum proteids depends on a portion of the globulin which can be precipitated by the addition of acetic acid to dilute serum. Casein after hydrolysis also yields no osazone. Such experiments show the importance and wide distribution of glucoproteids; all proteids, however, are not glucoproteids.

W. D. H.

Uroproteic Acid, a New Constituent of Urine. By Max Cloetta (*Chem. Centr.*, 1897, ii, 1154; from *Arch. exp. Path. Pharm.*, **40**, 29—39. Compare Töpfer, this vol., ii, 501).—To prepare uroproteic acid, dogs' urine is treated with calcium carbonate or baryta, the excess of the base removed by sulphuric acid or carbonic anhydride,

the filtrate made neutral or slightly alkaline, evaporated to a syrup, warmed with excess of barium hydroxide, and then treated with four times its volume of 95 per cent. alcohol. The coarse, flocculent, yellowish-brown precipitate of the basic barium salt thus obtained is filtered, washed with water, decomposed with sulphuric acid, the solution neutralised with barium carbonate, decolorised with animal charcoal, evaporated to a small volume, and treated with alcohol. Two grams of the barium salt was obtained from 4 litres of the urine of dogs which had been well fed on flesh. The formula of the acid deduced from analysis of the barium salt is probably $C_{66}H_{116}N_{20}SO_{54} + nH_2O$. This acid is a derivative of albumin, and does not give the biuret reaction. When decomposed with sulphuric acid, it yields a melanin-like substance, *uromelanin*, formic acid, carbonic acid, and ammonia. E. W. W.

Cytological Staining. By ALBERT MATHEWS (*Amer. J. Physiol.*, 1898, 1, 445—454).—The acid histological stains will combine with albumoses only in acid solutions ; under such circumstances, they form combinations similar to picric or other acid combinations with albumoses, and probably enter into one or more of the amido-groups in the albumose molecule. The basic stains will combine with albumoses only in alkaline solution, when they form insoluble, coloured compounds. The basic dyes react in this respect like basic lead acetate, protamine, histon, or other organic bases. The basic stains probably enter the hydroxyl of the phenol group of the albumose molecule, since they will not precipitate gelatin.

The staining of coagulated egg-albumin depends on chemical combinations similar in all respects to those which the albumoses enter into with the same stains. Freshly prepared hæmatoxylin will not stain tissues and, corresponding with this, will not precipitate the albumoses in either acid, neutral, or alkaline solutions. Hæmatein and sodium carminate react towards the albumoses and tissues like the acid stains. The aluminium salts of these stains, however, probably owing to the strong basicity of the metal, react like basic stains.

The affinity of microscopic sections for stains depends on reactions similar to the above. In slightly acid or neutral solutions, the basic dyes will stain any element of the tissue which contains an organic acid in a saline combination with a strong base ; hence their affinity for the chromatin of nuclei, in which a histon or protamine salt of nucleic acid is contained. Artificial nucleins are also stained by methyl-green so long as they are not saturated with albumin ; as soon as the acid becomes saturated with albumin, the nuclein shows a preponderating attraction for acid stains. This is evidence that the acid stain enters the albumin molecule, whilst the basic enters the nucleic acid molecule in these nucleins. W. D. H.

Hæmin Hydrochloride. By MAX ROSENFELD (*Chem. Centr.*, 1897, ii, 1153 ; from *Arch. exp. Path. Pharm.*, 40, 137—146).—According to the author, the composition of hæmin prepared from horses' blood by Cloetta's method (Abstr., 1896, i, 660) differs from that prepared by Cloetta from the blood of oxen only in containing 0·5 per cent. less of

hydrogen. When Nencki's method (Abstr., 1895, 69, 825) is modified so that the blood-powder is prepared by diluting with sodium sulphate solution before centrifugalising, a product whose content of nitrogen corresponds with Cloetta's formula, $C_{30}H_{34}N_3FeO_3$, is obtained. Hence the author assumes that Nencki's preparation contains a substance rich in nitrogen, and since phosphorus could be detected (by molybdate after fusing with sodium carbonate and potassium nitrate), this substance is probably nuclein derived from the colourless blood corpuscles. Hæmin, containing 3 atoms of nitrogen to 1 of iron, can be prepared as follows. Fresh oxen blood, after removing the fibrin, is mixed with a 2 per cent. solution of sodium sulphate and centrifugalised; the mass of corpuscles is freed from serum, again treated with sodium sulphate, centrifugalised, and then mixed with twice its volume of 96 per cent. alcohol, filtered after remaining 1—2 hours, and dried at the ordinary temperature. A solution of anhydrous oxalic acid in alcohol is added to 300—400 grams of the powder mixed with sufficient 96 per cent. alcohol to form a thin pulp, until the colour changes from red to brown. The filtrate, after remaining 24 hours, is again filtered, and a concentrated solution of hydrogen chloride in alcohol added drop by drop; the hæmin crystals, which at once begin to separate, are washed with alcohol, ether, and water, and then recrystallised from hot alcohol to which a solution of hydrogen chloride in alcohol is added. The content of chlorine is not constant, and the chlorine cannot be completely removed by washing with water. E. W. W.

Iodine in the Thyroid Gland. By R. TAMBACH (*Zeit. Biol.*, 1898, 36, 549—567).—The absolute quantity of iodine in the thyroids of pigs from different sources is fairly constant, but the amount of proteids that can be extracted varies considerably. The iodine-containing proteid compounds are almost completely extractable with water. These compounds are precipitable by reagents like acids, alcohol, &c., which precipitate proteids; only a small percentage (4) of the total iodine remains in solution; of this, half is present in compounds soluble in water, such as iodides; the remaining half is more firmly combined, but these combinations are also soluble in water. There is no free iodothyrin in the gland. By artificial gastric and pancreatic digestion of the iodine proteid compounds, iodothyrin is not separated, but digestive products are formed in which the iodine is combined in a similar way to that in which it is in the parent substance. Iodothyrin is only obtainable by destruction of the proteid molecule, and even then all the iodine is not present as iodothyrin; part passes into a peptone-like substance. The iodine, in fact, appears to be present in the form of several proteid compounds. The therapeutic activity of extracts of the thyroid is more probably associated with these proteid compounds of iodine or their digestive products than with iodothyrin.

W. D. H.

Iodothyrin. By ERNST ROOS (*Zeit. physiol. Chem.*, 1898, 25, 1—15).—The following elementary analyses of iodothyrin are given in percentages.

I. From sheep. II. From human thyroids; *a*, from Switzerland, *b*, from Kiel.

	I.	S.	N.	C.	H.	Cl.	Ash.
I.	4·31	1·40	8·91	58·24	7·43	0·4	0·40
II *a*.	1·31	1·40	10·41	61·41	8·06	0·52	—
II *b*.	2·58	1·40	10·03	57·04	7·28	0·5	0·47

These numbers show great discrepancies, especially in the percentage of iodine, which is particularly abundant in the iodothyrin of the sheep. Whether these differences are due to the mode of preparation, or indicate real individual differences between iodothyrin from various sources, is still uncertain. W. D. H.

Organic Chemistry.

Explosion of Mixtures of Methane by Electric Currents. By H. COURIOT and JEAN MEUNIER (*Compt. rend.*, 1898, **126**, 750—753). —An extensive series of experiments was made on the action (1) of incandescent wires or filaments, and (2) of electric sparks on mixtures of methane with various proportions of air, the gas being sometimes still and sometimes in motion.

A current of a mixture of 80 per cent. of methane and 20 per cent. of air could not be ignited by an incandescent wire or by the spark produced when the wire melted owing to the intensity of the current. In contact with a flame, however, the mixture readily ignited.

Whatever the proportion of air and methane, the only effect produced by an electric current, if it produces any effect at all, is an explosion. Under no circumstances, however, were the authors able to produce an explosion by means of an incandescent wire. When an explosion is produced, it is due to the breaking of the wire and the consequent production of a spark. The most readily explosive mixture contains 9·5 per cent. of methane. So long as the proportion of methane does not fall below 5·5 per cent., combustion during the explosion is complete. Slight explosions were observed with so low a proportion of methane as 4·5 per cent. The maximum limit of explosibility is 12 per cent. of methane, and the authors never obtained an explosion when the proportion was as high as 12·25 per cent.

C. H. B.

Ignition of Mixtures of Methane and Air by the Electric Spark. By H. COURIOT and J. MEUNIER (*Compt. rend.*, 1898, **126**, 901—904).—The authors have previously described experiments which show that mixtures of methane and air are not ignited by incandescent wires, but if the wires fuse and a spark is produced, ignition takes place (preceding abstract). They now find that if the current by which the wire is heated is shunted with a parallel shunt, the production of the spark causes no ignition when the resistances in the two branches are equal. If the resistance of the shunt is high, the production of a spark always leads to the ignition of the mixture of methane and air; on the other hand, when the resistance of the shunt falls below a certain value, the production of a spark likewise causes an explosion. In order to avoid an explosion, the intensity of the current must not exceed a certain maximum, which depends on the resistance of the two branches of the conductor. C. H. B.

Di-isopropyl in Light Petroleum from Baku. By OSSIAN ASCHAN (*Ber.*, 1898, **31**, 1801—1803. Compare this vol., i, 407).— It is shown experimentally that the fraction of Russian petroleum which boils at 57—59° consists of di-isopropyl. M. O. F.

Combination of Olefines with Mercury Salts. By GEORGES DENIGÈS (*Compt. rend.*, 1898, 126, 1145—1148).—The olefines generally, like butylene, combine with mercuric sulphate in acid solution, and yield compounds of the type $(SO_4Hg,HgO)_3R''$, in which R'' is an olefine; they are yellow compounds which dissolve readily in hydrochloric acid, especially on heating, and with effervescence if the particular olefine is gaseous at the ordinary temperature. A solution of 50 grams of mercuric oxide in 200 c.c. of sulphuric acid and 1000 c.c. of water may conveniently be used. The olefine, if gaseous, is passed into this solution, or if liquid, like trimethylethylene, is agitated with it. All three butylenes yield similar compounds, and that obtained from unsymmetrical dimethylethylene is more stable than the compound formed by trimethylethylene. The propylene compound is very unstable, and at 90—100° in contact with the mother liquor it is rapidly converted into mercuric sulphate and acraldehyde. C. H. B.

Purification of Acetylene. By A. BERGÉ and ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 218—221).—Acetylene, prepared from commercial calcium carbide, is contaminated with notable quantities of hydrogen sulphide and hydrogen phosphide. Both these impurities may be removed by passing the gas through bromine water, as recommended by Willgerodt, but this reagent rapidly becomes exhausted, is incapable of regeneration, and converts part of the acetylene into bromine derivatives. Hydrogen sulphide is best removed by means of caustic soda solution, and hydrogen phosphide by subsequently passing the gas through a solution of mercuric chloride acidified with hydrochloric acid, or through nitric acid containing a small quantity of a salt of copper or iron in solution. The precipitate produced in the mercuric chloride solution may be collected and dissolved in nitric acid; a little hydrochloric acid is then added, and the solution is ready for further use. By making use of these processes, the impurities may be quantitatively determined, the sulphur absorbed by the caustic soda being converted into sulphuric acid, and the phosphorus into phosphoric acid. Two samples of acetylene were thus found to contain, per cubic metre, 1032 and 1417 c.c. of hydrogen sulphide, and 945 and 985 c.c. of hydrogen phosphide. N. L.

Constitution and Synthetical Application of the Sesquihydrochloride of Hydrogen Cyanide. By LUDWIG GATTERMANN and K. SCHNITZSPAHN (*Ber.*, 1898, 31, 1770—1774).—The authors find that when "sesquihydrochloride of hydrogen cyanide," which was first prepared by Claisen and Matthews (*Ber.*, 1883, 16, 308), who represented it by the formula 2HCN,3HCl, is heated with benzene, a product is obtained which yields benzhydrylamine, $CHPh_2\cdot NH_2$, on hydrolysis with alcoholic potash. This fact, taken in conjunction with the formation of ethylic chloride, formic acid, and formamidine, when the sesquihydrochloride is heated with alcohol, renders it probable that the so-called sesquihydrochloride has the formula

$$NH:CH\cdot NH\cdot CHCl_2,HCl.$$

Benzhydrylformamidine hydrochloride, $NH:CH\cdot NH\cdot CHPh_2,HCl$, is prepared by adding aluminium chloride to a mixture of benzene with

the "sesquihydrochloride of hydrogen cyanide," and pouring the product into ice cold water containing a small quantity of hydrochloric acid; the *platinochloride* crystallises from dilute alcohol in yellow needles, and melts at 210°. The free *base* is crystalline, and melts at 118—120°; boiling, dilute caustic soda slowly eliminates ammonia, yielding formylbenzhydrylamine (Leuckart and Bach, Abstr., 1886, 1023), from which the base is obtained by the prolonged action of alkali.

The "sesquihydrochloride of hydrogen cyanide" acts still more vigorously on toluene, and the product yields tolhydrylamine (Goldschmidt and Stöcker, Abstr., 1891, 1479). Hexamethyltriamidotriphenylmethane, the leuco-base of "crystal-violet," is obtained by heating dimethylaniline with the "sesquihydrochloride of hydrogen cyanide" at 120—130° during 3 hours. M. O. F.

Preparation of Cyanogen Chloride. By ALFRED HELD (*Bull. Soc. Chim.*, 1897, [iii], 17, 287—290).—Numerous attempts to devise a more satisfactory method of preparing cyanogen chloride than that of saturating a solution of mercuric cyanide with chlorine, led to the adoption of the following process:—260 grams of potassium cyanide (after allowing for impurity) and 90 grams of crystallised zinc sulphate are dissolved in 8 litres of water, and chlorine is passed into the solution until the white precipitate of zinc cyanide, which is produced in the later stages of the operation, is nearly redissolved. If excess of chlorine has been used, it may be removed by adding a little potassium cyanide. The chlorine is rapidly absorbed, and the solution keeps well for a long time; it may be used immediately after being made, and there is no excess of chlorine to be got rid of, as in the usual process. Each litre of the solution contains at least 30 grams of cyanogen chloride. N. L.

Ammonio-compounds of Cuprosocupric Cyanide. By ERNST SCHMIDT (*Arch. Pharm.*, 1898, **236**, 246—248. Compare next abstract).—Twenty years ago, the author made the observation that when an ammoniacal solution of copper sulphate is nearly decolorised by adding potassium cyanide, and allowed to stand, deep green crystals of the composition $Cu_3(CN)_4,3NH_3$ separate. Denner assigned the same composition to a preparation made in a similar manner in the Marburg laboratory in 1884. Malmberg's results (see next abstract) show that a whole series of green cuprosocupric cyanide compounds, mentioned in literature, and to which various formulæ are assigned, possess in reality the same composition. The above-mentioned green ammonium compound of cuprosocupric cyanide takes up ammonia to form the blue *compound*, $Cu_3(CN)_4,4NH_3$, and by loss of ammonia is converted into a violet *salt*, $Cu_3(CN)_4,2NH_3$.

Under the same conditions as above, an ammoniacal nickel sulphate solution gives a violet-coloured salt. A. W. C.

Ammonio-cuprosocupric Cyanide. By EDWARD MALMBERG (*Arch. Pharm.*, 1898, **236**, 248—260. Compare preceding abstract).—The following analytical methods were used in this research. Copper was estimated partially as the sulphide by precipitation with hydrogen sulphide, and partially as the metal by heating the substance in an

atmosphere of hydrogen. For the estimation of cyanogen, the compound was distilled with dilute hydrochloric acid, and the liberated hydrogen cyanide received in dilute caustic soda solution and titrated with N/10 silver nitrate solution.

The ammonia was determined by distilling the substance with caustic soda, after addition of sodium sulphide to combine with the cyanogen. The distillate was collected in N/10 sulphuric acid, and after passing carbonic anhydride through the warmed solution to get rid of hydrogen sulphide, the excess of acid was titrated with N/10 caustic potash, using rosolic acid as indicator.

Green Ammonio-cuprosocupric Cyanide Compounds.—The green compounds obtained by Hilkenkamp (*Ann.*, 1859, **97**, 218) of the supposed composition $Cu(CN)_2 + 2Cu_2(CN)_2 + 4NH_3 + 2H_2O$; by Dufau (*J. pr. Chem.*, 1853, **59**, 498) of the composition $Cu_2(CN)_2 + Cu(CN)_2 + 4NH_3$; by Schiff and Bechi (*Ann.*, 1866, **138**, 24) of the composition $Cu(CN)_2 + 2Cu_2(CN)_2 + 6NH_3$; and by Fleurent (*Compt. rend.*, 1892, **114**, 1066) of the composition $Cu_2(CN)_2 + 2Cu(CN)_2 + 2NH_3 + 3H_2O$, are in reality all represented by the formula $Cu_3(CN)_4,3NH_3$.

Violet ammonio-cuprosocupric cyanide, $Cu_3(CN)_4,2NH_3$, is obtained by boiling the finely powdered green salt with water, or with water and a little ammonia, until a sample of the filtered mixture deposits violet crystals. This salt is not decomposed on exposure to the air.

Blue ammonio-cuprosocupric cyanide, $Cu_3(CN)_4,4NH_3$, is produced when the green salt is heated for some hours on the water bath with a mixture of solutions of ammonia and ammonium carbonate; it is less stable than the violet salt. The blue salts described by Hilkenkamp (*loc. cit.*), Dufau (*loc. cit.*), Fleurent (*loc. cit.*), Schiff and Bechi (*loc. cit.*), and Mills (*Chem. Centr.*, 1863, 154) have also this same composition.

Ammonio-cuprous Cyanide, $Cu_2(CN)_2,2NH_3$.—When preparing Fleurent's blue compound (*loc. cit.*), if the mixture be heated to 160—170° instead of 140—145°, a white substance is obtained of the above formula; it decomposes easily on exposure to the air, and in contact with ammonia passes into the violet, green, or blue compounds described above. A. W. C.

Decompositions of Alkylic Thiocyanates. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1898, **126**, 838—840).—When methylic thiocyanate is mixed with a solution of bleaching powder, there is little action in the cold, but, on warming, nitrogen and carbonic anhydride are liberated, and methylsulphonic acid is formed. A solution of sodium hypochlorite containing excess of sodium hydroxide acts less readily, and some sulphuric acid is formed in addition to the other products. Ethylic thiocyanate is much less readily attacked, and in this case also some sulphuric acid is formed. With a hot solution of sodium hypochlorite containing an excess of the hydroxide, the ethylic salt yields sodium ethylsulphonate and sodium cyanide, but if the action is allowed to continue after all the hypochlorite has been reduced, any excess of the ethylic thiocyanate is converted into ethylic bisulphide, sodium cyanide, and sodium cyanate. Amylic thiocyanate is only slightly attacked under similar conditions, but the products are analogous.

Methylene thiocyanate, when heated with a concentrated solution of bleaching powder, yields methylenedisulphonic acid, carbonic anhydride, and nitrogen; in presence of excess of alkali, hydrogen cyanide is formed in place of carbonic anhydride and free nitrogen, and traces of cyanic and sulphuric acids are also produced.

Allylic isothiocyanate is but slightly attacked, even in hot solutions; some nitrogen is liberated, and some sulphuric acid is produced.

C. H. B.

Remarks on the Action of Chlorine on Ethylic Alcohol. By André Brochet (*Bull. Soc. Chim.*, 1897, [iii], 17, 224—228).—The views of Fritsch and other observers are discussed, and the conviction is expressed that the formation of chlorinated acetals is due to secondary reactions, and is not an essential part of the process (see following abstract). N. L.

Theory of the Action of Chlorine on Ethylic Alcohol. By André Brochet (*Bull. Soc. Chim.*, 1897, [iii], 17, 228—230).—The chlorination of ethylic alcohol is comparable to that of the higher aliphatic alcohols studied by the author, and is to be explained in a similar manner. It appears that small quantities of ethylic acetate and monochlorethylic alcohol are first formed, but the limit of acidity below which these compounds can exist is soon attained, and from this time dichlorethylic alcohol, $CH_2Cl\cdot CHCl\cdot OH$, is constantly produced. The latter, under the dehydrating influence of hydrochloric acid, reacts with alcohol, according to the reaction of Wurtz and Frapolli, and gives rise to dichlorethylic oxide, $CH_2Cl\cdot CHCl\cdot OEt$, and, by the further action of chlorine, to trichlorethylic oxide, $CHCl_2\cdot CHCl\cdot OEt$. These compounds react with water to give alcoholates of chlorinated aldehydes, and with alcohol to give chlorinated acetals. The latter are decomposed, as the temperature rises, with re-formation of the chlorinated ethylic oxides, whilst the former are eventually converted into chloral alcoholate by the continued action of chlorine. N. L.

Combination of Trimethylcarbinol with Mercuric Nitrate. By Georges Denigès (*Compt. rend.*, 1898, 126, 1043—1045).—When trimethylcarbinol is boiled with a solution of mercuric nitrate, it yields an insoluble orange compound, which blackens when exposed to light; this explodes when struck or when heated to about 80°, is decomposed by hydrochloric acid, with liberation of unsymmetrical dimethylethylene and formation of mercurous and mercuric chlorides, and by hot solutions of alkali hydroxides with formation of mercurous and mercuric oxides. It does not contain a trimethylcarbinol group, and is to be regarded as a dimethylethylene mercurosomercuric nitrate, $NO_3Hg_2\cdot C_4H_8\cdot HgNO_3$. C. H. B.

Cholesterols from Lower Plants. By Ernest Gérard (*Compt. rend.*, 1898, 909—911).—The cholesterol obtained from cultures of *Staphylococcus alba* in peptonised beef broth differs from the cholesterols obtained from animals or higher plants. With concentrated sulphuric acid, it gives a blood-red coloration, which is not imparted to chloroform when the latter is shaken with the acid; if the sulphuric acid solution is diluted with water, it yields a greenish, and not a white,

precipitate; when a solution in carbon tetrachloride is agitated with concentrated sulphuric acid, the acid becomes blood-red, and the tetrachloride becomes green; if exposed to the air, it alters and becomes coloured.

The cholesterol from *Fucus crispus* behaves in the same way.

It follows that the cholesterols of microbes or of algæ belong to the group of ergosterols, and resemble the cholesterols obtained from cryptogams, but not those obtained from animals or the higher plants.

C. H. B.

Propionaldol. By August Thalberg (*Monatsh.*, 1898, **14**, 154—160).—*Propionaldol*, $C_6H_{12}O_2$, is formed when propaldehyde is allowed to remain in contact with a saturated solution of potassium carbonate, the whole being kept cool. It is a very viscid transparent liquid, which boils at 94—96° under a pressure of 23 mm. By reduction with aluminium amalgam, it is converted into the corresponding *glycol*, $CH_2Me{\cdot}CH(OH){\cdot}CHMe{\cdot}CH_2{\cdot}OH$, boiling at 214°, and readily yields an *oxime*, $C_6H_{12}O{:}NOH$; this is a thick, yellow liquid, which boils at 140° under a pressure of 22 mm. On gentle oxidation, the aldol yields propionic acid and a *hydroxyhexoic acid*, $CH_2Me{\cdot}CH(OH){\cdot}CHMe{\cdot}COOH$, which is a syrupy liquid and forms an anhydrous *barium* salt. More vigorous oxidation converts this acid into diethyl ketone.

A. H.

Acid Glycerophosphates. By Adrian and Auguste Trillat (*Compt. rend.*, 1898, **126**, 1215—1218).—The acid glycerophosphates, $[C_3H_5(OH)_2O{\cdot}PO(OH)O]_2M''$, may be prepared by decomposing the corresponding normal salts with the theoretical quantity of sulphuric acid, or by the double decomposition of the acid barium salt with a soluble sulphate. They are uncrystallisable, vitreous substances, readily soluble in water, from which they are precipitated with difficulty by alcohol. Although the potassium and sodium salts cannot be obtained free from water, the barium, zinc, calcium, magnesium, copper, and strontium salts become anhydrous at 120°. Aqueous solutions of acid glycerophosphates are decomposed on boiling, with formation of the normal salt, phosphoric acid and glycerol being liberated. The normal glycerophosphates of pyridine, aniline, phenylhydrazine, quinine, and cocaine have been prepared by agitating ethereal solutions of these bases with an aqueous solution of an acid glycerophosphate. These compounds will be described hereafter.

N. L.

Action of the Sorbose Bacterium on Polyhydric Alcohols. By Gabriel Bertrand (*Compt. rend.*, 1898, **126**, 762—765).—The conversion of sorbitol into sorbose, and of mannitol into levulose by the action of the sorbose bacterium, are analogous, since in both cases a ketose is produced by oxidation of a secondary alcoholic group in the original compound. The author has therefore investigated the action of the sorbose bacterium on various polyhydric alcohols. Glycol, xylitol, and dulcitol resist the oxidising action of the bacterium, and do not aid in its development. Glycerol, sorbitol, and mannitol (in which the number of carbon atoms is a multiple of three) favour the development of the bacterium, and are converted into reducing sugars

which contain two atoms of hydrogen less than the original alcohol. Erythritol, arabitol, volemitol, and perseitol belong to this second group, and behave in the same way. There is a well-marked stereochemical difference between the two groups, and it seems that those alcohols only are oxidised by the sorbose bacterium which contain a CH·OH chain arranged in such a manner that there is not a hydrogen atom on the same side as the hydroxyl group that is attacked in the oxidation.

Further investigations are being made. C. H. B.

Soluble Starch. II. By Wiktor Syniewski (*Ber.*, 1898, **31**, 1791—1796. Compare this vol., i, 61).—Soluble starch obtained by the author's method has the specific rotatory power $[\alpha]_D = 195·3°$ in a 10 per cent. solution at 20°.

Solutions of higher concentration than 12·5 per cent. become turbid from separation of an insoluble modification, which is formed from soluble starch through elimination of water. Baryta converts soluble starch into the *compound* $C_{18}H_{32}O_{16},BaO$.

The *acetyl* derivative, $C_{18}H_{25}O_9(OAc)_7$, is obtained by heating soluble starch with barium carbonate and acetic chloride in sealed tubes at 120°, and afterwards at 140°; it is a white, amorphous powder, and melts at 110—120°. The *benzoyl* derivative,

$$C_{18}H_{25}O_9(OBz)_7,$$

melts above 120°.

Inversion with hydrochloric acid converts soluble starch into 99·3 per cent. of the amount of dextrose required by the formula $C_{18}H_{32}O_{16}$. Water at 140—145° under pressure gives rise to only 3·99 per cent., whilst diastase produces maltose in quantities varying according to the temperature and duration of action. M. O. F.

Resolution of Starch by the Action of Diastase. By Henri Pottevin (*Compt. rend.*, 1898, **126**, 1218—1221).—The explanation of the conversion of starch into dextrin and maltose by a series of hydrolytic decompositions is not in accordance with the experiments of Brown and Heron, who find that the various dextrins are identical as regards composition, molecular weight, and rotatory power. A number of experiments are described which tend to show (1) that the conversion of starch into maltose takes place in two distinct stages. dextrin being the intermediate product; (2) that the difference between the various dextrins is merely one of physical state; (3) that the different parts of the starch granules differ in the ease with which they are converted into dextrin, and the dextrin thus formed into maltose. In consequence of this, when starch is acted on by diastase, the transformation proceeds with unequal rapidity in different portions of the mass, some parts having already been converted into maltose while others are still in the dextrin stage, or, perhaps, not yet attacked. N. L.

Action of the Silent Electric Discharge on Nitrogenous Carbon Compounds in presence of Free Nitrogen. By Marcellin P. E. Berthelot (*Compt. rend.*, 1898, **126**, 775—793).—Experiments were made with many different groups of carbon com-

pounds containing nitrogen. In the case of solid compounds, or liquids having a low vapour pressure, the action could not be pushed to its limit; in almost all cases, nitrogen was absorbed, and condensation products of the nature of polyamines, polyamides, and condensed derivatives were formed. The most notable exceptions to the general rule that nitrogen is absorbed are ethylamine, allylamine, phenylhydrazine, thiocarbamide, ethylenediamine and propylenediamine. Methylamine and nitromethane actually lose nitrogen, probably because in them the ratio of nitrogen to carbon is unity, whereas in the polyamines formed from mononitrogenous compounds it is less than unity. The diamines absorb practically no nitrogen. Compounds of the methane series lose hydrogen at the same time that they combine with nitrogen, the loss being of the same order as in the case of the hydrocarbons and alcohols of the same series. This loss of hydrogen is greatest with the monamines, but not so great with allylamine and ethylene- and propylene-diamines. The cyclic character of the product is more marked the higher the number of carbon atoms in the original compound, but to this general result certain highly oxygenised compounds form exceptions.

Pyrroline, indole, and other aromatic compounds lose no hydrogen when they combine with the nitrogen; pyridine, likewise, loses no hydrogen, but piperidine, on the other hand, loses a relatively large proportion, and tends to change into pyridine.

When the compositions of the polyamines formed from the hydrocarbons, alcohols, and amines are compared, it would seem that, for a given weight of nitrogen, the condensation of the hydrocarbon, for a given number of carbon atoms, increases from the hydrocarbon to the alcohol, and from the latter to the monamine. With diamines, the condensation is double what it is with monamines.

Isomerides, as a rule, behave similarly, but benzylamine and toluidine differ considerably in the amount of nitrogen with which they combine. Methylaniline behaves as if the methyl and phenyl groups acted separately, the two effects being superposed; this cumulative effect is important, and is seen still more distinctly when comparison is made between dimethylamine and ethylamine, trimethylamine, and the propylamines. In the case of amines, the quantity of nitrogen absorbed seems to be proportional to the number of alkylic residues in the amine.

The compounds formed by combination with nitrogen without elimination of hydrogen behave, as a rule, like amines or amides; it is clear that if they are saturated and non-cyclic compounds, they cannot be regarded as direct derivatives of the compound from which they have been formed. In the benzene series, for example, the products must be regarded as derived, not from benzene itself, but from its hydrides.

Albumin combines with a considerable proportion of nitrogen, with liberation of about an equal volume of hydrogen, together with some carbonic anhydride and carbonic oxide, and this result may be of importance in connection with the influence of atmospheric electricity on vital processes. C. H. B.

Ethylisoamylamines. By AUGUSTE DURAND (*Bull. Soc. Chim.*, 1897, [iii], 17, 405—408).—The pasty mass formed by the action of ethylic iodide on isoamylamine was dissolved in water and distilled with potash, the distillate being received in dilute hydrochloric acid. The secondary base was separated by means of its nitroso-derivative, which was then distilled with steam, and dried with calcium chloride.

Nitrosoethylisoamylamine, $C_5H_{11}\cdot NEt\cdot NO$, is a thick, golden-yellow liquid, slightly soluble in water, having a persistent, somewhat suffocating odour, and boiling at 144° under a pressure of 85 mm.

Ethylisoamylamine, $C_5H_{11}\cdot NHEt$, obtained by heating the preceding compound with concentrated hydrochloric acid and subsequently distilling with sodium carbonate, is a thick, colourless liquid of strong ammoniacal odour. It boils at 127° at the ordinary pressure, is slightly soluble in water, and has a sp. gr. = 0·764. The *platinochloride* crystallises in orange-red needles; the *aurochloride* is a syrupy liquid, crystallising with difficulty in small, orange-red needles; and the *oxalate* crystallises in tufts of silky needles.

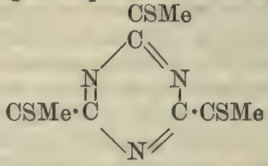
Diethylisoamylamine, $C_5H_{11}\cdot NEt_2$, is obtained by distilling with soda the residues from the preparation of ethylisoamylamine, and is identical with the product which Hofmann obtained by the decomposition of triethylisoamylammonium iodide. It is a thick, colourless liquid boiling at 155° (corr.), and having an odour recalling that of pyridine. The *picrate* forms fine yellow crystals melting at 75°.

N. L.

Diagnosis of Secondary Aliphatic Amines containing Monatomic Alkyl Groups. By ARMAND BERG (*Bull. Soc. Chim.*, 1897, [iii], 17, 297—300).—It has been shown in a previous note that secondary chloramines are decomposed by alcoholic potash with elimination of hydrogen chloride and formation of an ethylenic linking; isobutylchloramine, for example, yields isobutylisobutylideneamine, which, on hydrolysis, is converted into isobutylamine and isobutaldehyde. The case of an amine containing two different radicles has now been studied.

Ethylisoamylchloramine, $CHMe_2\cdot CH_2\cdot CH_2\cdot NClEt$, obtained by the action of sodium hypochlorite on ethylisoamylamine hydrochloride, is a yellowish, oily liquid of disagreeable odour, insoluble in water, boiling at 72° under 37 mm. pressure, and of sp. gr. 0·919 at 0°. When treated with rather more than the theoretical quantity of sodium dissolved in alcohol and finally mixed with water, an oily liquid separates which cannot be distilled without decomposition. On distillation with a slight excess of hydrochloric acid, a mixture of valeraldehyde and acetaldehyde passes over, whilst the residue, when distilled with potash, yields ethylamine and isoamylamine. It appears, therefore, that the decomposition of ethylisoamylchloramine takes place in both of the ways theoretically possible, with formation of isoamylethylideneamine, $CHMe_2\cdot CH_2\cdot CH_2\cdot N\colon CHMe$, or ethylisoamylideneamine, $CHMe_2\cdot CH_2\cdot CH\colon NEt$. On hydrolysis, the former yields isoamylamine and acetaldehyde, whilst the latter yields ethylamine and valeraldehyde. The constitution of the original base is thus clearly shown by the products obtained by the successive action of alcoholic potash and of acids. N. L.

Derivatives of Symmetrical Triazine. By JULIUS TROEGER and V. HORNUNG (*J. pr. Chem.*, 1898, [ii], **57**, 357—365).—Attempts to replace the chlorine atoms in solid α-dichlorocyanethine (hexachlorotriethylcyanidine) without breaking the triazine ring, by acting on it with moist silver oxide, silver carbonate, potassium acetate, or alcoholic potash, proved unsuccessful; but when it is treated with alcoholic potassium hydrogen sulphide, *trithioacetylcyanidine*



is obtained as a white, amorphous substance. It burns with great difficulty when heated on platinum foil, and is entirely decomposed on heating with concentrated acids.

Acetyldithioacetylcyanidine, $C_3N_3Ac(CSMe)_2$, produced by the action of alcoholic potassium sulphide on dichlorocyanethine, is an ochre-brown, amorphous substance possessing no melting point.

The great insolubility of both these sulphur compounds in all ordinary reagents renders their purification a matter of extreme difficulty; the only proof of their purity is afforded by the analytical numbers, for no evidence could be obtained from a study of their decomposition products. A. W. C.

Action of the Silent Electric Discharge on Aldehydes and Nitrogen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, **126**, 671—680).—The author continues his researches on the action of the silent electric discharge on mixtures of nitrogen with various carbon compounds, and in this paper describes the results of experiments with various compounds having an aldehydic function; acetaldehyde, propaldehyde, acetone, dimethylmethylal, aldol, paraldehyde, trioxymethylene, camphor, benzaldehyde, benzoin, cinnamaldehyde, salicylaldehyde, furfuraldehyde, quinone, glucose, cellulose, and humus. In all cases there is absorption of nitrogen, accompanied by liberation of hydrogen, the volume of which, however, is always considerably smaller than the volume of the nitrogen absorbed, and in the case of the polymerides of aldehyde, and of aldehydes of the benzene and campholic series, is very small indeed. The quantity of nitrogen absorbed is comparatively high in the case of primary aldehydes, ketones, quinone, camphor, and furfuraldehyde and compounds similar to dimethylmethylal, but is low in the case of the polymerides of aldehyde, benzoin, glucose, cellulose and its derivatives. With solids and the less volatile liquids, it is very difficult to obtain the maximum possible amount of change, owing to the low vapour pressures of the compounds.

The products are condensed compounds of the nature of amides or amines, and belong to the same class as the ammoniacal compounds of the aldehydes; they resemble more especially the glycosines, glyoxalines, and polyamines containing a low proportion of hydrogen.

Aldehyde absorbs less nitrogen than propaldehyde, and in this

reaction seems to behave like a methane derivative rather than like the higher homologues. Propaldehyde and acetone absorb practically the same proportion of nitrogen. The influence of polymerisation is uncertain, owing to the difficulty of reaching the limit of the reaction in the case of the polymerides.

In the case of isomerides such as propaldehyde and allylic alcohol, the former combines with more than twice as much nitrogen as the latter, whereas ethereal salts of dihydric alcohols combine with more nitrogen than the aldehydes with which they are respectively isomeric. The relative behaviour of isomeric aldehydes and acids, such as salicylaldehyde and benzoic acid, remains uncertain, because the limit of the reaction is very difficult to reach.

Acetaldehyde combines with rather less than one atom of nitrogen; propaldehyde and acetone with nearly three atoms; dimethylmethylal combines with an atom of nitrogen for each atom of carbon. In the case of the other compounds, the results are less definite, but the proportion of nitrogen absorbed is, as a rule, lower the more condensed the original molecule. C. H. B.

Commercial Preparation of Chloral. By AUGSUTE TRILLAT (*Bull. Soc. Chim.*, 1897, [iii], 17, 230—234).—The process is divided into three stages :—1. *Preparation of chloral alcoholate.*—Dry chlorine is passed into absolute alcohol contained in a large glass balloon connected by tubes with one or more vessels of water for absorption of the hydrogen chloride evolved. The temperature is at first kept low, but is afterwards, as the action becomes less violent, gradually raised to 100°. At the end of 10—14 days, the liquid is found to be completely soluble in water; the current of chlorine is then stopped, and, on cooling, a white, solid mass of chloral alcoholate is obtained. The action of the chlorine is facilitated by the addition of iodine (1 per cent.) to the alcohol, or by a little crystallised ferric chloride. 2. *Conversion of chloral alcoholate into chloral.*—The still liquid chloral alcoholate is transferred to an enamelled vessel and gradually mixed with an equal volume of concentrated sulphuric acid, the solution being then heated in a reflux apparatus until hydrogen chloride is no longer evolved. The mixture is then distilled until a temperature of 100° is reached, and the distillate is redistilled, the portion passing over below 94° constituting pure chloral. 3. *Conversion of chloral into chloral hydrate.*—The chloral is mixed with the theoretical quantity of water and the liquid run on to a smooth level surface to cool and solidify, or, if a purer product is required, the still liquid hydrate is mixed with about one-third of its volume of chloroform and allowed to crystallise in closed vessels. After about a week, the crystals are drained, and dried at the ordinary temperature. Benzene or carbon bisulphide may be used instead of chloroform. N. L.

Acetals of Acraldehyde and of Glyceraldehyde. By ALFRED WOHL (*Ber.*, 1898, 31, 1796—1801).—An acetal of acraldehyde has not yet been prepared, addition of alcohol occurring simultaneously

with acetal formation when the aldehyde is treated with alcohol; the substance can be obtained, however, by an indirect method.

Chloropropionaldehydediethylacetal, $CH_2Cl\cdot CH_2\cdot CH(OEt)_2$, is prepared by slowly adding acraldehyde to ice-cold, absolute alcohol saturated with hydrogen chloride; it was first obtained by Alsberg (*Jahresbericht*, 1864, 495) on saturating with hydrogen chloride a mixture of acraldehyde and alcohol.

Acraldehydeacetal, $CH_2\colon CH\cdot CH(OEt)_2$, which is formed on heating an intimate mixture of the foregoing substance with caustic potash, occurs in the fraction of the product which boils at 120—130°. It is a limpid oil, having a peculiar odour which is not unpleasant, and boils at 123·5° under a pressure of 762 mm.; its sp. gr. = 0·85425 at 15°. Cold dilute hydrochloric acid sets free acraldehyde from the acetal, and bromine gives rise to the dibromide (compare Claisen, this vol., i, 421).

Hydroxychloropropionacetal, $CH_2Cl\cdot CH(OH)\cdot CH(OEt)_2$, is produced by the action of hypochlorous acid on acraldehydeacetal; it is a colourless, somewhat viscous oil, and boils at 126° under a pressure of 32 mm.

Epihydrinaldehydeacetal, $CH(OEt)_2\cdot CH<\overset{CH_2}{\underset{O}{|}}$, is obtained by heating the foregoing substance with potash under reduced pressure; it boils at 165°.

Glyceraldehydeacetal, $OH\cdot CH_2\cdot CH(OH)\cdot CH(OEt)_2$, prepared from hydroxychloropropionacetal either by the action of aqueous potassium carbonate or by direct oxidation with potassium permanganate, is a colourless, viscous liquid, miscible with water and with alcohol, and having a burning taste. It boils at 130° under a pressure of 20·7 mm. Dilute mineral acids hydrolyse the substance very readily, giving rise to glyceraldehyde. M. O. F.

Product of the Oxidation of Glycerol by the Sorbose Bacterium. By GABRIEL BERTRAND (*Compt. rend.*, 1898, **126**, 842—844).—When the sorbose bacterium is allowed to grow in a solution of yeast containing 2 to 5 per cent. of glycerol, the latter is partially converted into dihydroxyacetone, identical with that obtained synthetically by Piloty (this vol., i, 117). It follows that the sorbose bacterium acts on glycerol in the same way as on sorbitol and mannitol, removing H_2 and forming a true ketose. C. H. B.

Biochemical Production of Dihydroxyacetone. By GABRIEL BERTRAND (*Compt. rend.*, 1898, **126**, 984—986).—Dihydroxyacetone is readily produced by the growth of the sorbose bacterium in broth containing 5 to 6 per cent. of glycerol. After removal of the gelatinous bacteroidal membrane, the liquid is distilled in a vacuum at the lowest possible temperature, and the residual syrup is mixed with five or six times its weight of absolute alcohol and two volumes of ether. The ether alcohol solution is drawn off and distilled at a low temperature under diminished pressure, when the residual liquor crystallises; after purification by washing with absolute alcohol, the dihydroxy-

acetone forms small hexagonal lamellæ. With sodium hydrogen sulphite, it forms a crystalline compound, from which it can again be separated in the usual way.

The yield of dihydroxyacetone under favourable conditions may amount to 30 per cent. of the weight of the glycerol taken.

C. H. B.

Action of Alkalis on Citral. Preparation of Methylheptenone. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1897, [iii], **17**, 175—193).—When citral is boiled for 12 hours with a solution of potassium carbonate in a reflux apparatus, it is quantitatively converted into acetaldehyde and methylheptenone. The latter boils at 168°, has a sp. gr. = 0·910 at 14°, and a refractive index $n_D = 1·437$ at 31°; it is identical with the methylheptenone obtained by other experimenters and synthesised by Barbier and Bouveault. Admitting the formula, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, proposed by these observers for methylheptenone, it follows that citral is 2 : 6-dimethyl-2 : 6-octadiene-8-al, $CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}COH$. The crude citral extracted from essence of lemon-grass by means of sodium hydrogen sulphite is a mixture of 90 per cent. of citral with 10 per cent. of methylheptenone. The latter may be separated by fractional distillation under diminished pressure, but complete purification is only to be effected by converting it into the oxime which has already been described; as prepared by the author, it boils at 120° under 25 mm. pressure, has a sp. gr. = 0·919 at 14°, and a refractive index $n_D = 1·475$ at 29°.

When methylheptenone and phenylhydrazine are mixed in molecular proportion, a *hydrazone* is produced, from which methylheptenone may be regenerated by the action of acids. If, however, the hydrazone be heated to about 130°, isomeric change takes place accompanied by a rise in temperature, and, on distillation, a yellowish oil, of sp. gr. = 0·985 at 0°, is obtained, which dissolves in acids without decomposition. This *compound* is also obtained by the action of phenylhydrazine on 2-methyl-6-heptanone-3-ol (see below), and must therefore be represented by the formula $CMe_2{:}CH{:}CH{<}{{CH_2{\cdot}CH_2}\atop{NPh—N}}{\gg}CMe$. When methylheptenone is shaken with hydrochloric acid, 2-*methyl*-2-*chloro*-6-*heptanone*, $CH_3{\cdot}CClMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, is formed, and the corresponding *bromine* and *iodine* derivatives are obtained by the action of hydrobromic and hydriodic acids. They are unstable liquids of pleasant, fruity odour, and are more easily prepared from trimethyldihydrohexone (see below), a cyclic isomeride of methylheptenone.

The main product of the action of concentrated sulphuric acid (75 per cent.) on methylheptenone is dihydrometaxylene [Me : Me : H : H = 1 : 3 : 5 : 6], previously obtained by Wallach by the action of zinc chloride on methylheptenone; it was identified by its physical properties and by its conversion into dinitrometaxylene. The action of chromyl chloride, in carbon bisulphide solution, on dihydrometaxylene was investigated. The principal product of the reaction is an unstable *chlorine* derivative, $C_8H_{11}Cl$, but metatolualdehyde is also formed.

With less concentrated sulphuric acid (40—50 per cent.), methylheptenone yields a tertiary alcohol, 2-methyl-6-heptanone-2-ol, and a secondary alcohol, 2-methyl-6-heptanone-3-ol, both having the empirical formula $C_8H_{16}O_2$.

2-Methyl-6-heptanone-2-ol, $CH_3\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot COMe$, may be obtained in crystals melting at 68°, but usually exists as an oily liquid having an odour of camphor, and boiling at 124° under 23 mm. pressure. With the halogen acids, it yields 2-chloro-, 2-bromo-, and 2-iodo-2-methyl-6-heptanone. The *hydrazone* is a thick, yellowish liquid boiling at 226° under 28 mm. pressure, and the *oxime* is a viscous syrup boiling at 172° under 32 mm. pressure. When distilled under the ordinary pressure, 2-methyl-6-heptanone-2-ol loses water and is converted into *trimethyldihydrohexone*, $CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH{=}CMe\end{matrix}>O$, isomeric with methylheptenone. It is a liquid of ethereal odour boiling at 129°, having a sp. gr. = 0·883 at 14°, and a refractive index $n_D = 1·470$ at 23°. When boiled for some time with water, it is converted into 2-methyl-6-heptanone-2-ol, whilst it dissolves in dilute sulphuric acid, giving a solution from which alkalis liberate the same compound. The halogen acids give rise to the same derivatives as are obtained from methylheptenone (see above). Bromine dissolved in methylic bromide yields a *compound* of the formula

$$CH_3\cdot CMeBr\cdot CH_2\cdot CH_2\cdot CBr\cdot COMe,$$

and having an extremely irritating odour, whilst with hydroxylamine the viscous oxime of 2-methyl-6-heptanone-2-ol is produced. On oxidation with potassium permanganate, trimethyldihydrohexone yields levulinic acid, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot COOH$, and, probably, also acetone.

2-Methyl-6-heptanone-3-ol, $CH_3\cdot CHMe\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot COMe$, boils at 127° under a pressure of 27 mm.; its sp. gr. is 0·950, and its refractive index $n_D = 1·456$ at 23°. With phenylhydrazine, it yields a compound identical with that obtained from methylheptenone, whilst heating with zinc chloride under reduced pressure converts 2-methyl-6-heptanone-3-ol into methylheptenone and dihydrometaxylene.

Synthesis of Methylheptenone.—Acetylpropylic alcohol, obtained by boiling with hydrochloric acid the product of the action of ethylenic bromide on ethylic sodacetoacetate, is treated with fuming hydriodic acid. The *iodide*, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2I$, thus obtained, having a sp. gr. = 1·391 at 0°, and boiling at 109—110° under 25 mm. pressure, is left in contact with excess of acetone and finely divided zinc for three months. The *tertiary alcohol*, $CMe_2(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot COMe$, produced in this reaction yields, on dry distillation, a small quantity of trimethyldihydrohexone which is then converted, by successive treatment with hydriodic acid and caustic soda, into 2-methyl-2-heptene-6-one. N. L.

Action of the Silent Electric Discharge on Organic Acids and Nitrogen. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, **126**, 681—691).—Experiments were made with acetic, propionic, and formic acids, methylic formate, ethylic formate, and methylic acetate, crotonic, benzoic, succinic, maleic, fumaric, orthophthalic, camphoric,

glycollic, lactic, malic, tartaric, hydroxybenzoic, pyruvic, levulinic, and dehydracetic acids and ethylic acetoacetate.

As a rule, the acids combine with nitrogen under the influence of the discharge; two molecules of acetic or propionic acid combine with three atoms of nitrogen; in other cases, the limit of the reaction was not reached, owing to the low vapour pressure of the acid. As a rule, hydrogen was liberated either in very small quantity or not at all, and in this respect the acids differ from the aldehydes. The liberation or non-liberation of hydrogen seems to be connected with the quantity and function of the oxygen contained in the compound; it is less with aldehydes than with alcohols, and much less with acids than with aldehydes. As a rule, there is little or no formation of carbonic oxide or carbonic anhydride, and therefore the whole of the oxygen remains in the compound formed; maleic and pyruvic acids are, however, exceptions, and yield carbonic oxide, whilst glycollic acid yields carbonic anhydride. Formic acid also yields carbonic oxide and carbonic anhydride, but in other ways also it behaves differently from other acids of the same series, probably because it is decomposed by the discharge; only a very small quantity of nitrogenous product is formed, and this is due to a secondary reaction. The alkylic formates absorb a considerable quantity of nitrogen, and yield both carbonic oxide and carbonic anhydride, due probably to the fact that the acidic and alkylic groups each react in their own special way with the nitrogen under the influence of the discharge. Analogous phenomena are observed when the behaviour of the alkylic formates is compared with that of their isomerides, such as propionic acid. The existence of two groups of reactions, which take place almost independently, is a specially noteworthy point.

Another remarkable result is the great difference in the behaviour of maleic and fumaric acids; the latter absorbs no nitrogen, and liberates neither carbonic anhydride nor carbonic oxide, whereas the former absorbs a considerable quantity of nitrogen and liberates a considerable quantity of carbonic oxide, mixed with some carbonic anhydride.

The rate at which the various monobasic and dibasic acids, whether of simple or complex function, absorb nitrogen, varies considerably, and depends on the constitution and physical condition of the particular acid. Fumaric acid is quite exceptional in absorbing no nitrogen at all.

Olive oil absorbs traces of nitrogen only, but is converted into a peculiar, white, gelatinous polymeride, insoluble in ether or alcohol.

C. H. B.

Hydrated Sodium Formate. By ALBERT COLSON (*Bull. Soc. Chim.*, 1897, [iii], 17, 165).—If, in Berthelot's synthesis of sodium formate, the temperature be about 20°, the anhydrous salt is produced, whereas at 0°, long, orthorhombic needles are formed having the composition $C_2HNaO_2 + 4H_2O$. N. L.

Solid Acetic Peroxide. By ALBERT COLSON (*Bull. Soc. Chim.*, 1897, [iii], 17, 165).—On evaporating an ethereal solution of acetic peroxide in a vacuum, it is obtained in hard crystals melting at 27° and slowly subliming at the ordinary temperature without melting. It detonates with violence when warmed. N. L.

Solidifying Points of Pure Stearic and Palmitic Acids, and of their Mixtures. By L. E. O. de Visser (*Rec. Trav. Chim.*, 1898, **17**, 182—189. Compare Heintz, *Ann. Phys. Chem.*, **92**, 588).—The solidifying point of stearic acid is 69·32°, or 69·247° on the scale of the hydrogen thermometer, and of palmitic acid 62·618°, or 62·532° on the hydrogen thermometer. The following table gives the solidifying points of mixtures of the two.

Per cent. stearic acid.	Solidifying point.	Per cent. stearic acid.	Solidifying point.	Per cent. stearic acid.	Solidifying point.
100	69·32°	48	56·40°	37	55·75°
90	67·02	47	56·40	36	55·62
80	64·51	46	56·39	34	55·38
70	61·73	45	56·38	32	55·12
60	58·76	44	56·36	30	54·85
55	57·20	43	56·31	29	54·92
54	56·85	42	56·25	25	55·46
53	56·63	41	56·19	20	56·53
52	56·50	40	56·11	15	57·80
51	56·44	39	56·00	10	59·31
50	56·42	38	55·88	0	62·618
49	56·41				

These numbers differ somewhat from those obtained by Heintz, but the latter are undoubtedly incorrect, as the capillary tube method was employed.

The results have been mapped out in the form of a curve which exhibits two breaks, one corresponding with a mixture containing 54 per cent. of stearic acid, and the other with a mixture containing 47·5 per cent. of stearic acid. This second break indicates that when a mixture containing 47·5 per cent. of stearic acid solidifies, both solid and liquid portions have the same composition. J. J. S.

Unsymmetrical Dimethylsuccinic Acid and its Alkylic Salts. By Edmond E. Blaise (*Compt. rend.*, 1896, **126**, 753—755).—Unsymmetrical dimethylsuccinic acid is obtained by the action of ethylic sodiomalonate on ethylic bromisobutyrate, hydrolysis of the resulting alkylic salt, and decomposition by heat of the tricarboxylic acid thus produced. Some α-methylglutaric acid is formed at the same time, but the production of this acid is minimised by using xylene as the solvent instead of alcohol.

The dimethylsuccinic acid was mixed with ten times its volume of absolute alcohol containing 1 per cent. of hydrochloric acid, and the mixture heated for some time in a reflux apparatus; the product was titrated with a solution of sodium ethoxide, the alcohol distilled off, and the residue diluted with water and agitated with light petroleum. The latter removes the normal salt, which can be obtained by evaporation, after drying the solution over anhydrous sodium sulphate. The results, as compared with those given by succinic acid under the same conditions, are as follows.

	Duration of reaction.	Alkyl salt. Normal.	Acid.	Free acid.
Succinic acid	10 hours	6·36	1·57	—
	20 ,,	6·59	0·99	—
	30 ,,	6·86	0·54	—
Dimethylsuccinic acid	10 ,,	0·49	0·34	1·82
	20 ,,	1·27	3·68	0·98
	30 ,,	2·19	3·23	0·68

With dimethylsuccinic acid, as with succinic acid, the two carboxyls are not alkylised simultaneously, and it would seem that the acid function of the one is increased by the presence of the other, so that, as one becomes alkylised, the other becomes less and less readily attacked. Where the acid is unsymmetrical, the energies of the two functions are very different, the tertiary carboxyl being much less readily alkylised than the primary carboxyl. On the other hand, the limit of alkylisation seems to be practically identical in the two cases. There seems to be no constant relation between the proportions of normal and acid alkylic salts formed at various stages of the reaction.

The different rates of formation of normal and acid salts make it comparatively easy to ascertain whether a substituted succinic acid is symmetrical or unsymmetrical. On the other hand, the two acid functions of dimethylsuccinic acid show no differences of the same order as those observed by Friedel in the case of camphoric acid.

C. H. B.

New Synthesis of ββ-Dimethylglutaric Acid. By Edmond E. Blaise (*Compt. rend.*, 1898, **126**, 1153—1155).—According to Fichter and Herbrand (Abstr., 1896, i, 643) methylsuccinic anhydride, when reduced with sodium amalgam, yields a lactone, $\begin{matrix}CHMe\cdot CO \\ | \\ CH_2-CH_2\end{matrix}\!>\!O$; but it is now shown that unsymmetrical dimethylsuccinic anhydride, when reduced in a similar manner, yields $\begin{matrix}CMe_2\cdot CH_2 \\ | \\ CH_2-CO\end{matrix}\!>\!O$, a colourless liquid boiling at 207—210°. This liquid is heated with finely divided potassium cyanide for 5 hours at 275—280° in sealed tubes, the product is dissolved in water, and after the unaltered lactone has been extracted with ether, the boiling aqueous solution is saturated with hydrogen chloride, evaporated to dryness, and the residue extracted several times with ether; the ethereal solution deposits ββ-dimethylglutamic acid, $COOH\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CONH_2$, in crystalline needles melting at 146°. This amic acid is not hydrolysed when boiled with concentrated hydrochloric acid, but when heated with alkalis yields ββ-dimethylglutaric acid (Perkin and Goodwin, Trans., 1894, 64, and Auwers, Abstr., 1895, i, 410).

J. J. S.

Action of Dilute and Concentrated Alkalis on *d*-Tartaric Acid. By J. Boeseken (*Rec. Trav. Chim.*, 1898, **17**, 224—230).—Holleman has shown (this vol., i, 515) that concentrated sodium hydroxide converts *d*-tartaric acid into racemic and mesotartaric acids. The author now shows that less concentrated alkali yields mesotartaric

acid. Racemic acid can be formed, not only directly from *d*-tartaric acid, but also from mesotartaric acid; this transformation is, however, reciprocal, since racemic acid, when boiled with sodium hydroxide, is partially converted into mesotartaric acid. J. J. S.

Condensation of Ethylic Acetonedicarboxylate with Ethylic Orthoformate. By GIORGIO ERRERA (*Ber.*, 1898, 31, 1682—1692). —It has been shown by Claisen that the action of ethylic orthoformate on ethereal salts of β-ketonic acids proceeds in one of two directions, according as acetic chloride or acetic anhydride is employed as the condensing agent, and the first of these changes has been studied in the case of ethylic acetonedicarboxylate (Abstr., 1896, i, 463). The author finds that when the latter substance combines with ethylic orthoformate under the influence of acetic anhydride, ethylic ethoxymethyleneacetonedicarboxylate, $OEt\cdot CH{:}C(COOEt)\cdot CO\cdot CH_2\cdot COOEt$, and ethylic diethoxymethyleneacetonedicarboxylate,

$$CO[C(COOEt){:}CH\cdot OEt]_2,$$

are produced; these compounds have not been actually isolated, but their existence is indicated by the nature of the products formed by the action of ammonia. Furthermore, the two ethereal salts interact in molecular proportion, yielding ethylic methenyl-bisacetonedicarboxylate, $COOEt\cdot CH_2\cdot CO\cdot C(COOEt){:}CH\cdot CH(COOEt)\cdot CO\cdot CH_2\cdot COOEt$, which undergoes internal condensation, forming ethylic hydroxytrimesate.

Ethylic hydroxytrimesate, $CH{<}{\begin{matrix}C(COOEt){:}C(OH)\\C(COOEt)\text{——}CH\end{matrix}}{>}C\cdot COOEt$, is obtained in the following manner. Ethylic acetonedicarboxylate (1 mol.), ethylic orthoformate (1 mol.), and acetic anhydride (2 mols.), are boiled in a reflux apparatus during 1 hour, and the portion which boils above 120° is then treated with concentrated, aqueous ammonia; a considerable proportion of a reddish-yellow precipitate separates during the next few hours, and this product, when dry, yields two substances on recrystallisation from benzene. Ethylic hydroxytrimesate is the more readily soluble, and crystallises from hot alcohol in colourless needles melting at 83°.

Ethylic 2 : 4-*dihydroxypyridine*-5-*carboxylate* (*dihydroxynicotinate*),

$$N{<}{\begin{matrix}C(OH)\text{===}CH\\CH\cdot C(COOEt)\end{matrix}}{>}C\cdot OH,$$

the less soluble substance, crystallises from water in lustrous, white needles, and from benzene in leaflets; it melts and decomposes at 213°. The *barium* derivative is crystalline, and contains $6H_2O$. The *acetyl* derivative crystallises from alcohol in lustrous, white needles, and melts at 147—148°. The *bromo*-derivative, $C_8H_8NBrO_4$, obtained by the action of bromine water, crystallises from alcohol in white needles; it becomes yellow when exposed to light, and blackens at 225°. 2 : 4-*Dihydroxypyridine*-5-*carboxylic* (*dihydroxynicotinic*) *acid* is prepared by the action of alkalis on the ethylic salt; it crystallises from water in microscopic needles and melts at 310°. The *bromo*-derivative, $C_6H_4NBrO_4$, separates from alcohol as a crystalline powder; it chars at 250°, but does not melt.

2 : 4-*Dihydroxypyridine*, $N{<}^{C(OH)\cdot CH}_{CH{=\!=}CH}{>}C\cdot OH$, is obtained from dihydroxynicotinic acid or its ethereal salt by heating it with concentrated hydrochloric acid at 160° for 2 hours, and subsequently at 190—200°; it melts and decomposes at 260—265°, and separates from alcohol in lustrous, transparent crystals belonging to the rhombic system; $a:b:c = 0{\cdot}6134:1:1{\cdot}29473$. The base is almost insoluble in ether, and dissolves very sparingly in cold water or alcohol; the aqueous solution is feebly acidic, and develops a reddish-brown coloration with ferric chloride. The *dibromo*-compound, $C_5H_3NBr_2O_2$, crystallises from water in colourless needles, and chars at 225—240°. The *ethylic* ether (*diethoxypyridine*), which is prepared by the action of ethylic iodide on the silver derivative, boils at 230—232°; it is heavier than water, is very volatile in an atmosphere of steam, and has an intense odour of pyridine. The *platinochloride* crystallises from alcohol in orange needles, and the *mercurichloride* in colourless needles melting at 167°. The *dibenzoyl* derivative of dihydroxypyridine crystallises from dilute alcohol in lustrous leaflets, and melts at 103°.

Ethylic 4-*pyridone*-3 : 5-*dicarboxylate*, $NH{<}^{CH:C(COOEt)}_{CH:C(COOEt)}{>}CO$, is prepared by heating ethylic acetonedicarboxylate (1 mol.), ethylic orthoformate (2 mols.), and acetic anhydride (4 mols.) in a reflux apparatus during 1 hour, and treating the fraction of the product which boils above 140° with alcoholic ammonia. The precipitate is a mixture of ethylic dihydroxynicotinate with the ammonium derivative of ethylic hydroxytrimesate. The mother liquor, on evaporation, yields ethylic pyridonedicarboxylate, which crystallises from alcohol in lustrous needles, and melts at 251°. When heated with concentrated hydrochloric acid at 165°, it yields the *acid*, which melts and decomposes at 315°; at a still higher temperature (210—215°), the action of hydrochloric acid gives rise to γ-pyridone. M. O. F.

Some Furfuran Derivatives. By PAUL FREUNDLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 419—424).—Attempts were made to prepare furfuranamine, $C_4OH_3{\cdot}NH_2$; by the action of bromine and potash on pyromucamide; by the decomposition of pyromucic hydrazide; and by the reduction of nitrofurfuran. Of the methods indicated, the last named alone was successful, and the results obtained by it will be subsequently described.

When pyromucamide is treated with bromine, a mixture of bromine additive products appears to be formed, whilst part of the amide suffers complete decomposition. No better results were obtained by the use of a solution of alkali hypobromite containing a very slight excess of bromine. Since Hofmann's reaction appears not to have been applied to aromatic amides, the behaviour of benzamide and cinnamamide was studied. The former, as was found by Linebarger (Abstr., 1894, i, 332), is first converted into benzoylbromamide,

$$C_6H_5{\cdot}CO{\cdot}NHBr,$$

from which, by warming with 30 per cent. sodium hydroxide solution, aniline is readily obtained. Cinnamamide, on the other hand, yields

a red additive product, $CHPhBr\cdot CHBr\cdot CO\cdot NH_2Br_2$, which is converted by the action of soda into *β-bromocinnamylbromamide*, $CHPh\colon CBr\cdot CO\cdot NHBr$; and this, by further treatment with alkalis, is decomposed, with liberation of ammonia. β-Bromocinnamylbromamide crystallises, when pure, in colourless needles melting at 188°.

When heated for some hours with hydrazine hydrate, ethylic pyromucate is converted into *pyromucic hydrazide*, $C_4OH_3\cdot CO\cdot NH\cdot NH_2$, which forms colourless scales melting at 30° and soluble in water and alcohol. *Pyromucazide*, $C_4OH_3\cdot CO\cdot N_3$, obtained by the action of sodium nitrite in acetic acid solution on the hydrazide, crystallises from chloroform in scales melting at 90°, and detonating when heated a little above that temperature. When heated with ethylic alcohol, it is quantitatively converted into the *urethane*, $C_4OH_3\cdot NH\cdot COOEt$, which could not be crystallised; the corresponding *methylic* derivative forms small prisms melting at 135°. The urethane was completely decomposed by hydrochloric acid, and, on heating with ammonia, only a few drops of a basic liquid, boiling at about 150°, were obtained; a quantity insufficient for purification and identification. N. L.

Oxidation of some Amides and Thioamides. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1898, **126**, 907).—Acetamide is not affected by dilute solutions of hypochlorites, but is oxidised by strong solutions, with liberation of nitrogen. The reaction is readily observed with a warm, concentrated solution of bleaching powder.

Thiocarbamide is less readily attacked than carbamide by an alkaline solution of sodium hypochlorite, and the decomposition is represented by the equation $CSN_2H_4 + 7O = CO_2 + SO_3 + N_2 + 2H_2O$. Phenylcarbamide is decomposed by the same reagent, especially on heating. Phenylthiocarbamide is much less readily attacked, the reaction in the early stages being $2NH_2\cdot CS\cdot NHPh + 11O = 2CO_2 + 2SO_3 + H_2O + N_2 + 2Ph\cdot NH_2$.

Sarcosine is slowly attacked by hot solutions of hypochlorites, whilst ethylic oxamate is decomposed slowly in the cold, and more rapidly on heating, the products being nitrogen, carbonic anhydride, water, and alcohol. C. H. B.

Yield of Carbamide obtained from Ammonium Carbonates. By LÉON BOURGEOIS (*Bull. Soc. Chim.*, 1897, [iii], **17**, 474—477).—Ammonium sesquicarbonate coarsely powdered was heated in a sealed tube at about 130° for 6 hours, the tube was then opened to relieve the pressure, and the operation of heating, &c., repeated until there was no longer any evolution of gas on opening the tube. On dissolving the contents of the tube in water and evaporating the solution to dryness, a residue of carbamide was obtained, which, in a series of experiments, ranged from 3·2 to 9·5 per cent. of the weight of ammonium sesquicarbonate employed. Ammonium bicarbonate and ammonium carbamate, when treated in a similar manner, yield respectively 2·5—2·9 and 2·6—3·7 per cent. of carbamide. In one experiment, in which 600 grams of ammonium sesquicarbonate were heated in a steel autoclave, the metal was found to be attacked, with formation of much ferrous carbonate, and 45·3 grams (7·55 per cent.) of carbamide was obtained. N. L.

Occurrence of Methylpentamethylene in Light Petroleum from the Caucasus. By OSSIAN ASCHAN (*Ber.*, 1898, 31, 1803—1806. Compare Markownikoff, Abstr., 1897, i, 401).—The fraction of Caucasian naphtha which boils at 71°, and has the sp. gr. = 0·7145 at 20°/4°, yields succinic and acetic acids, showing that the hydrocarbon oxidised is methylpentamethylene; nearly 7 per cent. of nitrobenzene is also produced. M. O. F.

Application of Ortho-xylylenic Bromide in Characterising Bases. By MAX SCHOLTZ (*Ber.*, 1898, 31, 1707—1709. Compare this vol., i, 383, 471, and 567).—According to their behaviour towards ortho-xylylenic bromide, amines may be divided into the following eight groups.

1. Primary aliphatic amines, which yield xylyleneimines (dihydroisoindoles), $C_6H_4{:}(CH_2)_2{:}NR$.

2. Secondary aliphatic amines, forming ammonium bromides of the type $C_6H_4{:}(CH_2)_2{:}NBrR_2$.

3. Tertiary aliphatic amines, which combine with a half molecular proportion of xylylenic bromide, yielding diammonium bromides of the type $C_6H_4(CH_2{\cdot}NBrR_3)_2$.

4. Primary aromatic amines, having the ortho-positions unoccupied; these behave like primary aliphatic amines, but the products are not basic (this vol., i, 383).

5. Primary aromatic amines with a substituent in the ortho-position; these yield derivatives of xylylenediamine having the constitution $C_6H_4(CH_2{\cdot}NHR)_2$.

6. Primary aromatic amines having both ortho-positions occupied do not combine with ortho-xylylenic bromide.

7. Secondary aromatic amines, which give rise to derivatives of xylylenediamine having the constitution $C_6H_4(CH_2{\cdot}NR_2)_2$.

8. Tertiary aromatic amines are indifferent towards ortho-xylylenic bromide. M. O. F.

Hexethylbenzene. By PAUL JANNASCH and A. BARTELS (*Ber.*, 1898, 31, 1716—1718).—By a simple method, details of which will be given later, the authors have obtained hexethylbenzene from benzene, ether, and aluminium chloride.

Diamidotetrethylbenzene is obtained by reducing with tin and hydrochloric acid the dinitro-derivative produced by the action of nitric acid on hexethylbenzene in presence of sulphuric acid; it melts at 92°, and forms large, white crystals which become pink, and finally reddish-brown in air. When boiled with ferric chloride, it yields a *compound* which melts at 56° and has the odour of quinone.

M. O. F.

Attempts to Prepare $\alpha\alpha\beta$-Triphenylethane. By J. RAWITZER (*Bull. Soc. Chim.*, 1897, [iii], 17, 477—480).—Unsuccessful attempts were made to prepare $\alpha\alpha\beta$-triphenylethane, $CH_2Ph{\cdot}CHPh_2$, (1) by the action of benzene, in presence of aluminium chloride, on chlorethylenic chloride, $CH_2Cl{\cdot}CHCl_2$; (2) by the action of benzene and aluminium chloride on bromodiphenylethane, $CH_2Ph{\cdot}CHBrPh$; (3) by the action of sodium on a mixture of benzylic chloride and bromo-

diphenylmethane, $CHBrPh_2$. Only dibenzyl was obtained by the first method, whilst from the products of the third reaction diphenylmethane, stilbene, tetraphenylethylene, and tetraphenylethane were isolated. As regards the second method, considerable difficulty was met with in the preparation of bromodiphenylethane, which Marquardt obtained by the action of bromine on diphenylethane. The sole product of this reaction at high temperatures appears to be solid dibromodiphenylethane, whilst the liquid product, presumably containing bromodiphenylethane, obtained at a low temperature, is of variable composition, and decomposes on distillation, with formation of dibenzyl, stilbene, and paradibromobenzyl. It yielded only dibenzyl when treated with benzene in presence of aluminium chloride.

N. L.

Action of Oxidising Agents on Nitrogen Compounds. By William Oechsner de Coninck (*Compt. rend.*, 1898, **126**, 1042—1043).—The author has continued his observations on the action of hypochlorites on amines and other nitrogen compounds. Hydroxylamine is immediately decomposed; methylamine hydrochloride decomposes slowly in the cold, and rapidly when gently heated; ethylamine hydrochloride is decomposed only when heated; aldehyde ammonia, when heated, yields methane and aldehydine, with a small quantity of nitrogen; aldoxime is readily decomposed in the cold; ethylenediamine, diethylenediamine, and propylenediamine are slightly decomposed, with liberation of nitrogen; the phenylenediamines are partially decomposed, the para-derivative being distinctly the most stable; guanidine is rapidly decomposed, and this is true also of hydrazine hydrochloride, phenylhydrazine, and phenylmethylhydrazine. Cyanuric acid also is rapidly decomposed. Piperidine, nicotine, sparteine, cocaine, ecgonine, and benzoylecgonine are not affected, but antipyrine yields a small quantity of nitrogen. C. H. B.

Combination of Organic Bases with Metallic Salts. By D. Tombeck (*Compt. rend.*, 1898, **126**, 967—970. Compare Abstr., 1897, 463, 560).—Aniline combines with cadmium, magnesium, zinc, and cupric sulphates to form compounds of the type $M''SO_4,2NH_2Ph$, which form small crystals, and decompose when heated. Nickel sulphate forms the compound $MSO_4,6NH_2Ph$, and cobalt sulphate a compound, $CoSO_4,4NH_2Ph$.

Cadmium, zinc, and magnesium nitrates form crystalline compounds of the same type, and the acetates seem to behave similarly.

Orthotoluidine and paratoluidine likewise form compounds with metallic sulphates, and these will be described later. C. H. B.

Melting Points and Boiling Points of Aniline, Toluidine, and Xylidine Hydrochlorides. By Fritz Ullmann (*Ber.*, 1898, **31**, 1698—1700).—The hydrochlorides of aniline, the toluidines, and the xylidines have definite melting points and boiling points, which are collected in the table on the following page.

The salts undergo no change on distillation, which has no influence on the melting point, or on the properties of the free base. It is

	M.p.	B. p. (728 mm.)	B. p. (760 mm.)
Aniline	198°	243°	245°
Orthotoluidine	214·5—215	240·2	242·2
Metatoluidine	228	247·8	249·8
Paratoluidine	243	255·5	257·5
Ortho-xylidine [Me : Me : NH_2=1 : 2 : 3]	254	256	258
Ortho-xylidine [Me : Me : NH_2=1 : 2 : 4]	256	264	266
Meta-xylidine [Me : Me : NH_2=1 : 3 : 4]	235	253·1	255·1
Para-xylidine [Me : Me : NH_2=1 : 2 : 4]	228	245·4	247·4

possible to recognise 2 per cent. of paratoluidine in a specimen of the ortho-base by determining the boiling point of the mixed hydrochlorides; the detection of a small quantity of the para-base has, hitherto, been a matter of some difficulty. M. O. F,

Xylylenediamines: an Undecatomic Ring. By MAX SCHOLTZ (*Ber.*, 1898, 31, 1700—1707. Compare this vol., i, 305, 565).—The author has shown that secondary amines, NHR_2, combine with orthoxylylenic bromide, forming substituted ammonium bromides of the type $C_6H_4\colon(CH_2)_2\colon NR_2Br$, and that these, acting on another molecule of the amine, yield the xylylenediamines, $C_6H_4(CH_2\cdot NR_2)_2$. It is now found that if ammonia is allowed to act on these ammonium bromides at 200° for 10 hours, bromine is replaced by the amido-group, giving rise to bases of the type $C_6H_4(CH_2\cdot NHR)_2$. This action may be even applied to xylylenepiperidonium bromide,

$$C_6H_4\colon(CH_2)_2\colon NBr\colon(CH_2\cdot CH_2)_2\colon CH_2,$$

which is thereby converted into the compound

$$C_6H_4<\begin{matrix}CH_2\cdot NH\cdot CH_2\cdot CH_2\\ CH_2\cdot NH\cdot CH_2\cdot CH_2\end{matrix}>CH_2,$$

containing eleven atoms in the ring. The production of secondary bases is not, however, without exception: xylylenediethylammonium bromide yields 2′-ethyldihydroisoindole, $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>NEt$.

Pentamethylene-xylylenediamine, $C_6H_4<\begin{matrix}CH_2\cdot NH\cdot CH_2\cdot CH_2\\ CH_2\cdot NH\cdot CH_2\cdot CH_2\end{matrix}>CH_2$, prepared by heating xylylenepiperidonium bromide with concentrated ammonia at 200° for 10 hours, boils at 180—182° under a pressure of 20 mm. The *nitroso*-derivative crystallises in transparent needles, and melts and intumesces at 104°. The *benzenesulphonamide* crystallises from alcohol in colourless prisms, and melts at 132°.

Pentamethylene-xylylenediamine diammonium bromide,

$$C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>NBr<\begin{matrix}CH_2\text{------}C_6H_4\text{------}CH_2\\ CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\end{matrix}>NBr<\begin{matrix}CH_2\\ CH_2\end{matrix}>C_6H_4,$$

is obtained by heating pentamethylene-xylylenediamine with ortho-xylylene bromide and alcoholic potash; the crystalline substance is hygroscopic, and melts at 65°. The *chloride* yields a *platinochloride* and an *aurichloride* which crystallise in microscopic needles. The *perbromide* is a yellow, crystalline powder.

Xylylenedi-isobutyl-diamine, $C_6H_4(CH_2\cdot NH\cdot C_4H_9)_2$, produced on

heating xylylene-di-isobutylammonium bromide with ammonia at 200° during 10 hours, is a colourless oil, and boils at 188—190° under a pressure of 20 mm. The *benzenesulphonamide* crystallises in lustrous prisms, and melts at 157°. The *diammonium bromide*, $C_6H_4[CH_2\cdot N(C_4H_9)Br\colon(CH_2)_2\colon C_6H_4]_2$, forms hygroscopic leaflets melting at 57°.

2'-*Ethyldihydroisoindole*, $C_6H_4<\substack{CH_2 \\ CH_2}>NEt$, prepared by heating xylylenediethylammonium bromide with ammonia, boils at 219—220° under atmospheric pressure. The *hydrochloride* is precipitated in needles on adding ether to the alcoholic solution; the *platinochloride* melts at 192°. The *methiodide* melts at 165°, and dissolves very readily in water and alcohol. Ethyldihydroisoindole is also obtained by the action of ethylamine on ortho-xylylenic bromide. M. O. F.

Oxidation of Hydroxylaminocarvoxime. By CARL D. HARRIES (*Ber.*, 1898, **31**, 1810—1812).—Hydroxylaminocarvoxime is prepared by the action of hydroxylamine (2 mols.) on carvone; the *picrate* melts at 150—151°.

Oxidation with mercuric oxide converts it into the *compound* $C_{10}H_{16}N_2O_2$, which melts at 153—155° and has the properties of a dioxime; at the same time, a substance is produced melting at 194° and having the property of reducing Fehling's solution.

When the dioxime is treated with boiling dilute sulphuric acid, hydroxylamine is eliminated, and the *compound* $C_{10}H_{14}O_2$ is formed; this crystallises in lustrous prisms, and melts at 193—194°. The constitution of this substance is represented by the formula

$$CHMe<\substack{CO\cdot CH_2 \\ CO\cdot CH_2}>CH\cdot CMe\colon CH_2.$$

M. O. F.

Rearrangement of β-Mesityloxime. By CARL D. HARRIES and RICHARD GLEY (*Ber.*, 1898, **31**, 1808. Compare this vol., i, 400).—When the aqueous solution of β-mesityloxime hydrochloride is boiled, it becomes turbid, and subsequently clear; the product is the hydrochloride of diacetonehydroxylamine. M. O. F.

Distinction between Magenta S and Ordinary Magenta, in Schiff's Reaction. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1897, [iii], **17**, 196—199).—The author replies to the criticisms of Lefèvre, and maintains that a solution of magenta S (the sodium salt of rosanilinetrisulphonic acid), decolorised by sulphurous acid, has its colour restored on adding pure alcohol, but is not affected by aldehyde unless a large excess of the latter be added. There is, therefore, an essential difference between magenta S and ordinary magenta, in this reaction.

N. L.

Reduction of Colouring Matters of the Type of Rosaniline and Malachite-green. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, [iii], **17**, 376—378).—Colouring matters of the type of rosaniline and malachite-green, when completely reduced with zinc dust and acetic acid, are converted into leuco-bases, the colour of which is not restored on exposure to air. If, however, the reduction be effected rapidly and

in the cold, the colour is restored on exposure to air or on boiling, but never attains the intensity of the original tint. This phenomenon is attributed to the fixation of two atoms of hydrogen by each amido-group, resulting in the formation of colourless derivatives of the type $CCl(C_6H_4{\cdot}NH_4)_3$, analogous to those obtained with the mineral acids (Abstr., 1893, i, 332). In the case of basic colouring matters of a different type, such as safranine, methylene-blue, and rhodamine, the original colour is restored in all its intensity by exposing to the air the products of reduction in the cold, the change taking place more quickly if the reduction has been effected by boiling. N. L.

The Supposed Tetrahydrochloride of Leucaniline. A Reply to Miolati. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1897, [iii], **17**, 193—196).—The analyses of Miolati are discussed, and the results are shown to be, in reality, more in accordance with the formula of the trihydrochloride, as maintained by the author, than with that of the supposed tetrahydrochloride. N. L.

Azophenols derived from Wroblewski's Bromoparatoluidine [Br:Me:NH$_2$ = 1 : 3 : 6]. By JOHN THEODORE HEWITT and HENRY E. STEVENSON (*Ber.*, 1898, **31**, 1782—1785).—*Bromotolueneazophenol*, [Br : Me : N$_2$ = 1 : 3 : 6], crystallises from dilute acetic acid in bright yellow leaflets, and melts at 104°; it contains $\frac{1}{2}H_2O$, and becomes anhydrous at 70°. The *acetyl* and *benzoyl* derivatives melt at 84—85° and 137—139° respectively; the *benzenesulphonate* crystallises from alcohol in orange leaflets and melts at 115°.

Bromotolueneazo-α-naphthol, [Br : Me : N$_2$ = 1 : 3 : 6], separates in red crystals on adding petroleum to its solution in chloroform; it melts at 160°. The *acetyl* and *benzoyl* derivatives melt at 155° and 150° respectively.

Bromotolueneazosalicylic acid, [Br : Me : N$_2$ = 1 : 3 : 6], melts at 228°, and the *methylic* and *ethylic* salts at 134° and 116° respectively.

M. O. F.

Action of Acetaldehyde on Phenylhydrazine. Two Isomeric α- and β-Triethylidenediphenylhydrazones. By HENRI CAUSSE (*Bull. Soc. Chim.*, 1897, [iii], **17**, 234—249).—The very variable results obtained by the author, and the indefinite character of the compounds prepared by Fischer, led him to suppose that the reaction between aldehyde and phenylhydrazine is not so simple as at first sight appears, and the whole subject has therefore been reinvestigated, with the following results.

When a solution of aldehyde is gradually added to a solution of phenylhydrazine made alkaline with baryta water, an unstable, crystalline substance melting at 53—55° is obtained, which appears to be a molecular combination of phenylhydrazine with another substance (*α-diphenyltriethylidenehydrazone*) melting at 60°.

In acid solution, substances are produced having melting points ranging from 68° to 80° and consisting of mixtures of the two isomeric α- and *β-diphenyltriethylidenehydrazones* in which the α-, or more fusible, derivative predominates.

In neutral solutions, on the other hand, a mixture melting at about 90° is obtained, the greater part of which consists of the β-, or less fusible, isomeride.

These substances give the same analytical results, corresponding with the empirical formula $C_{18}H_{22}N_4$, but are distinguished, and separated, from each other by their behaviour towards solvents, the α-compound, of lower melting point, being more soluble in alcohol and less soluble in water than the β-compound.

α-Diphenyltriethylidenehydrazone is best prepared in the pure state by slowly adding aldehyde dissolved in normal phosphoric acid to a solution of phenylhydrazine and sodium thiosulphate. The crystals which separate are washed with small quantities of water and alcohol and recrystallised from the latter. Obtained in this way, α-diphenyltriethylidenehydrazone forms colourless, hygroscopic needles melting at 60°, slightly soluble in cold water but readily dissolved by hot water and by most organic solvents. On exposure to air, it rapidly increases in weight and becomes yellow and red; it is decomposed by mineral acids in the cold and also by acid chlorides; alkalis, however, are without action. With benzaldehyde, it yields colourless needles of *diphenyldibenzylidenehydrazone*, $C_{23}H_{24}N_4$, melting at 156°; whilst with pyrogallol an unstable crystalline *compound*, of low melting point, is produced.

β-Diphenyltriethylidenehydrazone is most suitably prepared by gradually adding a solution of aldehyde to a solution of phenylhydrazine phosphate to which some glycerol has been added to moderate the action. A granular deposit is formed from which alcohol dissolves out α-diphenyltriethylidenehydrazone, whilst the residue, when recrystallised from hot alcohol, yields colourless, prismatic crystals of the β-compound melting at 99·5°. The latter is quite stable, remaining unaltered on exposure to air or light; it is insoluble in cold water but slightly soluble in hot water, alcohol, ether, and benzene. It is not affected by concentrated mineral acids in the cold and is only partially decomposed by them on heating, with formation of aldehyde and phenylhydrazine. Alkalis, acid chlorides, benzaldehyde, and pyrogallol are without action on β-diphenyltriethylidenehydrazone.

As to the constitution and mode of formation of the compounds described, it is suggested that the interaction of aldehyde and phenylhydrazine first results in the formation of diphenylethylidenedihydrazone, $CHMe(NPh\cdot NH_2)_2$, which is then converted, by the further action of aldehyde, into either α-diphenyltriethylidenehydrazone, $CHMe(NPh\cdot N\colon CHMe)_2$, or β-diphenyltriethylidenehydrazone,

$$CHMe\begin{matrix}\diagup NPh\text{---}N\diagdown \\ CHMe< \\ \diagdown NPh\text{---}N\diagup\end{matrix}CHMe.$$

The latter closed-chain formula is considered to be more in accordance with the great stability of the β-compound. N. L.

Unsymmetrical Phenylhydrazine Derivatives. By HANS RUPE (*Annalen*, 1898, 301, 55—58. Compare Abstr., 1897, i, 409).—Although ethylic chloracetate yields symmetrical derivatives of phenylhydrazine when allowed to act on the base, chloracetamide chloracetanilide, and chloracetyldimethylparaphenylenediamine give rise to unsymmetrical phenylhydrazido-compounds (compare following abstracts). M. O. F.

Unsymmetrical α-Phenylhydrazidoacetanilide. By HANS RUPE and GEORG HEBERLEIN (*Annalen*, 1898, **301**, 58—69. Compare Abstr., 1895, i, 521).—The compound obtained from phenylhydrazidacetanilide and ethylic acetoacetate crystallises from alcohol in slender needles, and melts at 147°. Concentrated sulphuric acid converts it into 1 : 3-*phenylmethyl-5-ketotetrahydropyridazine-4-carboxylic acid*,

$$CMe\begin{matrix}\diagup CH(COOH)\cdot CO \diagdown \\ \diagdown N\text{———————}NPh \diagup\end{matrix}CH_2,$$

which crystallises in white needles, and melts and decomposes at 230°.

The *acetyl* derivative of phenylhydrazidacetanilide (compare Widman, Abstr., 1893, i, 411) melts at 169·5°.

Diphenyldiketotetrahydrotriazine, $CH_2\begin{matrix}\diagup NPh\cdot NH \diagdown \\ \diagdown CO\cdot NPh \diagup\end{matrix}CO$, prepared by the action of carbonylic chloride on phenylhydrazidacetanilide dissolved in chloroform, melts at 257—258°; it is insoluble in acids, and dissolves with difficulty in alkalis. M. O. F.

Unsymmetrical Phenylhydrazidacetamide. By HANS RUPE, GEORG HEBERLEIN, and ARMAND ROESLER (*Annalen*, 1898, **301**, 69—75).—*Unsymmetrical phenylhydrazidacetamide*,

$$NH_2\cdot NPh\cdot CH_2\cdot CO\cdot NH_2,$$

is obtained by heating chloracetamide with an alcoholic solution of phenylhydrazine (2 mols.); it dissolves readily in alcohol, which allows it to be separated from α-phenylhydrazido-β-acetophenylhydrazine, produced in equal quantity. It melts at 150°, and the *benzylidene* compound at 225°.

Anilidacetamide (*phenylglycinamide*), $NHPh\cdot CH_2\cdot CO\cdot NH_2$, was first prepared by P. J. Meyer (*C. Soc. J.*, 1876, i, 373); it is most conveniently obtained by heating chloracetamide with alcohol and aniline, and after crystallisation from alcohol melts at 133°. The *nitroso*-derivative forms yellow needles, and melts at 145°; reduction with zinc dust and acetic acid converts it into unsymmetrical phenylhydrazidacetamide (m. p. 150°).

α-Phenylhydrazido-β-acetophenylhydrazine,

$$NH_2\cdot NPh\cdot CH_2\cdot CO\cdot NH\cdot NHPh,$$

is produced in equal quantity with unsymmetrical phenylhydrazidacetamide by the action of chloracetamide on phenylhydrazine; it crystallises from alcohol in lustrous, white leaflets, and melts at 178°. It is also formed when phenylhydrazidacetamide is heated with phenylhydrazine; the *benzylidene* compound melts at 196°. M. O. F.

Unsymmetrical Phenylhydrazidacetoparamidodimethylaniline. By HANS RUPE and JOS. VŠETEČKA (*Annalen*, 1898, **301**, 75—79. Compare Abstr., 1897, i, 409).—*Chloracetoparamidodimethylaniline*, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot NMe_2$, prepared by the action of chloracetic chloride on paramidodimethylaniline, crystallises from alcohol in slender, white needles, and melts at 146—147°.

Unsymmetrical phenylhydrazidacetoparamidodimethylaniline,

$$NH_2\cdot CPh\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot NMe_2,$$

obtained by the action of the foregoing substance on phenylhydrazine dissolved in alcohol, crystallises in yellow needles or leaflets, and melts at 134—135°. The *benzylidene* compound melts at 184—185°,

and the *acetyl* derivative, which crystallises in nacreous leaflets, melts at 158°; the *compound* with ethylic acetoacetate melts at 185°.

Phenylglycineparamidodimethylaniline,

$$NHPh\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot NMe_2,$$

is produced by the action of chloracetoparamidodimethylaniline on aniline, and melts at 122—134°; the *nitroso*-derivative crystallises in white needles melting at 165°, and does not give Liebermann's reaction. M. O. F.

Unsymmetrical α-Phenylhydrazido-α-acetophenylhydrazide. By Hans Rupe, Georg Heberlein, and Armand Roesler (*Annalen*, 1898, **301**, 79—88).—*Phenylglycinacetophenylhydrazide*,

$$NHPh\cdot CH_2\cdot CO\cdot NPh\cdot NHAc,$$

is prepared by the action of aniline on α-chloraceto-β-acetophenylhydrazine, and melts at 141°; 10 per cent. sulphuric acid hydrolyses it to *phenylglycinephenylhydrazine*, which crystallises from alcohol in white needles and melts at 153—154°.

Nitrosophenylglycinacetophenylhydrazide,

$$NO\cdot NPh\cdot CH_2\cdot CO\cdot NPh\cdot NHAc,$$

crystallises from alcohol in yellow needles and melts at 98°. *Unsymmetrical phenylhydrazidaceto-β-acetophenylhydrazide*,

$$NH_2\cdot NPh\cdot CH_2\cdot CO\cdot NPh\cdot NHAc,$$

obtained by the reduction of the foregoing compound with zinc dust and acetic acid, crystallises from alcohol in cubes melting at 176°; the *benzylidene* derivative melts at 184°.

Unsymmetrical phenylhydrazido-α-acetophenylhydrazide,

$$NH_2\cdot NPh\cdot CH_2\cdot CO\cdot NPh\cdot NH_2,$$

obtained by hydrolysing the acetyl derivative with 10 per cent. sulphuric acid, crystallises from dilute alcohol or from benzene in small, white needles melting at 155°; the *dibenzylidene* and *diacetyl* derivatives melt at 180—181° and 198° respectively. The *compound* $C_{14}H_{16}N_4O_2$ is produced by the action of carbonylic chloride on phenylhydrazido-α-acetophenylhydrazide; it crystallises from dilute alcohol in small, white needles, and melts at 209—210°.

M. O. F.

α-Orthamidobenzophenylhydrazide. By Hans Rupe and Armand Roesler (*Annalen*, 1898, **301**, 89—94).—*α-Orthonitrobenzo-β-acetophenylhydrazide*, $NO_2\cdot C_6H_4\cdot CO\cdot NPh\cdot NHAc$, is prepared by heating acetophenylhydrazide dissolved in benzene with orthonitrobenzoic chloride in a reflux apparatus; it crystallises from benzene in white needles, and melts at 134°. According to the reducing agent employed, two different products are obtained from this substance.

α-Orthamidobenzo-α-acetophenylhydrazide,

$$NH_2\cdot C_6H_4\cdot CO\cdot NPh\cdot NHAc,$$

is produced by the action of zinc dust and acetic acid, and crystallises from hot water in large, lustrous crystals melting at 140°; the *benzylidene* compound forms colourless needles, and melts at 175—177°.

α-Orthamidobenzophenylhydrazide, $NH_2\cdot C_6H_4\cdot CO\cdot NPh\cdot NH_2$, prepared by reducing the nitro-compound with stannous chloride and hydrochloric acid, also crystallises from water in large, lustrous prisms melting at 134°; the *platinochloride* forms microscopic, yellow

needles, and is somewhat unstable. The *dibenzylidene* and *diacetyl* derivatives melt at 150—151° and 195—196° respectively. The *compound* $C_6H_4<\begin{matrix}CO\cdot NPh\\ NH\text{—}CO\end{matrix}>NH$, produced by the action of carbonylic chloride on orthamidobenzophenylhydrazide, crystallises from hot chloroform in slender needles and melts at 218—219°. M. O. F.

Pulegonehydroxylamine. By CARL D. HARRIES and GEORG ROEDER (*Ber.*, 1898, **31**, 1809—1810).—Pulegoneoxime hydrate (Beckmann and Pleissner, Abstr., 1891, 936) should be called *pulegonehydroxylamine*, being a cyclic analogue of diacetonehydroxylamine; its constitution is expressed by the formula

$$CHMe<\begin{matrix}CH_2\text{—}CO\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2\cdot NH\cdot OH.$$

Oxidation converts it into nitrosomenthone and nitromenthone, which melt at 35° and 80° respectively. M. O. F.

Benzylidenediphenylhydrazines and their Derivatives. Transformation into Dibenzylidenediphenyltetrazole. By HENRI CAUSSE (*Bull. Soc. Chim.*, 1897, [iii], **17**, 480—485).—*Tribenzylidenediphenylhydrazine*, $CHPh\left<\begin{matrix}N\text{———}NPh\\ >CHPh\quad\quad\\ N\text{———}NPh\end{matrix}\right>CHPh$, is produced by the interaction of benzaldehyde and phenylhydrazine in aqueous or dilute alcoholic solution. It forms colourless, microscopic crystals, insoluble in water, benzene, and chloroform, but slightly soluble in alcohol. *Dibenzylidenetriphenylhydrazine*,

$$CHPh\left<\begin{matrix}N\text{———}NPh\\ >CHPh\quad\quad\\ N\text{———}NPh\end{matrix}\right>C_6H_8N_2,$$

obtained by treating benzaldehyde with phenylhydrazine in presence of alcohol and acetic anhydride, crystallises in colourless, microscopic needles, insoluble in water, somewhat soluble in alcohol. The *antimonite*, $CHPh\left<\begin{matrix}N\text{———}NPh\\ >CHPh\quad\quad\\ N\text{———}NPh\end{matrix}\right>Sb\cdot OH$, obtained by the action of benzaldehyde on a solution of phenylhydrazine antimonyl tartrate containing excess of antimonious acid, forms colourless needles which become red on exposure to light. The *arsenite*,

$$CHPh\left<\begin{matrix}N\text{———}NPh\cdot As(OH)_2\\ >CHPh\quad\quad\quad\quad\quad\\ N\text{———}NPh\cdot As(OH)_2\end{matrix}\right.,$$

is prepared in a similar manner. All the compounds described are decomposed by heat, or by boiling with alcohol, with formation of dibenzylidenediphenyltetrazole melting at 154°. N. L.

Influence of Distance Action exerted by Substituents on the Formation of Tetrazolium Bases. By EDGAR WEDEKIND and LEO STAUWE (*Ber.*, 1898, **31**, 1746—1757. Compare this vol., i, 192). —When formazyl derivatives undergo internal condensation and yield tetrazolium bases, substituents attached to the formyl carbon-atom exert a more marked influence than those replacing hydrogen in

a benzene nucleus. In other words, the influence of X in the system

$$\cdot CX\left\langle\begin{array}{l}N\cdot NPh\\ \quad\vdots\\ N\cdot NPh\end{array}\right.$$

is greater than that of X and Y in the system

$$C\left\langle\begin{array}{l}N\cdot N\cdot C_6H_4X\\ \quad\vdots\\ N\cdot N\cdot C_6H_4Y\end{array}\right. ;$$

the nitro-group, occupying an ortho-position, is, however, an exception to this generalisation.

The action of the following substituents of formyl hydrogen, arranged in order of increasing influence, has been studied: CN, Ph, COOEt, COPh, N:NPh, COMe, Me, COOH, and H; the yield of tetrazolium base consequently diminishes in the same order, falling from the theoretical amount in the case of cyano-compounds, to 20 per cent. when there has been no replacement of hydrogen.

In studying the behaviour of formazyl compounds containing a substituent in one of the benzene groups, the velocity of reaction was so great that it became necessary to study compounds into which a carboxylic group had been already introduced as a retarding agent, compounds of the general formula $C_6H_4X\cdot N\colon N\cdot CPh\colon N\cdot NH\cdot C_6H_4\cdot COOH$. It was then found that the groups, NO_2, COOH, COH, COMe, and SO_3H exerted the greatest influence, whilst the substituents, Me, Et, Pr^β, and chlorine displayed unimportant differences in their retarding effect. An orthonitro-group retards more strongly than the same substituent in the meta- and para-positions, which do not differ from one another very considerably in action (compare Bischoff, this vol., i, 131); the influence of ortho-chlorine is unimportant, and the carboxylic groups occupy an intermediate position, in the increasing order, para, meta, and ortho.

Formazylbenzenedicarboxylic acid,

$$(m)\ COOH\cdot C_6H_4\cdot NH\cdot N\colon CPh\cdot N\colon N\cdot C_6H_4\cdot COOH\ (o),$$

prepared from metabenzylidenehydrazonebenzoic acid and diazotised orthamidobenzoic acid, separates from acetone and water as a pale red, crystalline powder melting at 225°. The *acids* from metamidobenzoic and paramidobenzoic acids melt at 214° and 218° respectively.

Formazylbenzenemetacarboxylic acid,

$$(m)\ COOH\cdot C_6H_4\cdot NH\cdot N\colon CPh\cdot N\colon NPh,$$

is obtained from metabenzylidenehydrazonebenzoic acid and diazotised aniline; it crystallises from alcohol in beautiful, reddish-black needles, and melts at 202°. Oxidation converts it into *triphenylmetacarboxytetrazolium* chloride, which yields the *iodide* melting at 217°.

Orthochloroformazylbenzenemetacarboxylic acid,

$$(m)\ COOH\cdot C_6H_4\cdot NH\cdot N\colon CPh\cdot N\colon N\cdot C_6H_4Cl\ (o),$$

crystallises from acetone in reddish-black needles and melts at 217°.

Orthonitroformazylbenzenemetacarboxylic acid,

$$(m)\ COOH\cdot C_6H_4\cdot NH\cdot N\colon CPh\cdot N\colon N\cdot C_6H_4\cdot NO_2\ (o),$$

prepared from metabenzylidenehydrazonebenzoic acid and diazotised orthonitraniline, crystallises from acetone in ruby-red needles and melts at 150°. *Metanitroformazylbenzenemetacarboxylic* and *paranitroformazylbenzenemetacarboxylic acids* melt at 185° and 165—170° respectively.

Xylylformazylbenzene, orthotolylformazylbenzene, and *cumidylformazylbenzene* melt at 137°, 154—155°, and 173—174° respectively.

Methyldiphenyltetrazolium *platinochloride,* which is a yellowish powder insoluble in all media excepting phenol, blackens at 220°, and melts at 238—239°. M. O. F.

Action of Chlorine on Ethers of Phenol and of β-Naphthol. By A. CURATOLO (*Gazzetta*, 1898, **28**, i, 154—159).—*Phenylic chlorosalicylate,* $COOPh\cdot C_6H_3Cl\cdot OH$ [OH : Cl = 2 : 5], obtained by passing chlorine into an alcoholic solution of salol, crystallises in colourless needles melting at 81—83°, and on hydrolysis with potash yields 5-chlorosalicylic acid melting at 171°. On passing chlorine into an acetic acid solution of salol, *phenylic dichlorosalicylate,*

$$COOPh\cdot C_6H_2Cl_2\cdot OH\ [OH : Cl_2 = 2 : 3 : 5],$$

is obtained; this crystallises in colourless needles melting at 115—116°, and on hydrolysis with potash yields the 3 : 5-dichlorosalicylic acid melting at 214°.

Monochloro-β-naphthylic dichlorosalicylate, $C_{10}H_6Cl\cdot OOC\cdot C_6H_2Cl_2\cdot OH$, is obtained by the action of chlorine on an alcoholic solution of betol; it crystallises in yellowish needles melting at 155—157°, and on hydrolysis with potash yields 3 : 5-dichlorosalicylic acid and 1-chloro-2-naphthol melting at 69—70°. Its constitution is thus defined. On chlorination in acetic acid solution, betol yields a mixture of dichloronaphthylic 3 : 5-dichlorosalicylates melting sharply at 192—197°; on hydrolysis with potash, it yields a mixture of dichloro-β-naphthols, melting at 95—105°.

On chlorinating β-naphthylic benzoate in alcoholic or acetic acid solution, a liquid *tetrachloro*-derivative, $C_{17}H_8Cl_4O_2$, is obtained; this boils at 178—180°, and on hydrolysis with potash yields 2 : 5-dichloro-1-benzoic acid. W. J. P.

Chlorine Derivatives of Phenylic Carbonate. By ETIENNE BARRAL (*Compt. rend.*, 1898, **126**, 908—909).—*Chlorophenylic carbonate,* $CO(OC_6H_4Cl)_2$, is obtained by placing in a large flask a solution of phenylic carbonate in carbon tetrachloride containing a small quantity of iodine, and filling the upper part of the flask repeatedly with chlorine. The reaction is somewhat energetic, but the presence of iodine is indispensable. The product, which crystallises in colourless, silky needles, melts at 142°, is insoluble in water, and only slightly soluble in cold benzene or alcohol, but very soluble in these liquids at their boiling points.

If the chlorine is passed into the carbon tetrachloride solution containing iodine (or antimony pentachloride) higher chlorine derivatives of the phenylic carbonate are produced, and these will be described later. C. H. B.

Migration of Chlorine from the Side-chain to the Ring on the Decomposition of Aromatic Iodochlorides: Derivatives of Anisidine. By PAUL JANNASCH and W. HINTERSKIRCH (*Ber.*, 1898, **31**, 1710—1714).—*Orthiodanisoil* is prepared from orthanisidine by the Sandmeyer reaction, and boils at 237—238°; its *dinitro*-derivative crystallises from alcohol in colourless, silky needles melting at 89°.

Anisoil iodochloride, $OMe\cdot C_6H_4\cdot ICl_2$, separates in lemon-yellow

crystals when chlorine is passed into a solution of iodanisoil in chloroform. Hydrogen chloride is liberated spontaneously from this substance in dry air, and if decomposition is allowed to proceed in the atmosphere, it changes completely to a dark brown liquid, which crystallises if cooled artificially and stirred persistently with a glass rod; it consists of *chloriodanisoil* [Cl : I : OMe = 5 : 2 : 1], which separates from aqueous alcohol in large, colourless crystals and melts at 48°. Chloriodanisoil is also produced when anisoil iodochloride is agitated with a solution of potassium iodide, one atomic proportion of iodine being set free. When chlorine is passed into a chloroform solution of chloriodanisoil, the *iodochloride* of chloranisoil is obtained, and crystallises from carbon bisulphide in yellow, transparent plates; when carefully dried, it may be preserved for weeks without undergoing decomposition, and chlorine does not migrate into the ring.

Iodosoanisoil, $OMe \cdot C_6H_4 \cdot IO$, prepared by the action of caustic soda on anisoil iodochloride, is a colourless substance, and liberates iodine from hydriodic acid. The action of steam converts it into *iodoxyanisoil*, $OMe \cdot C_6H_4 \cdot IO_2$. M. O. F.

Migration of Chlorine from the Side-chain to the Ring on the Decomposition of Aromatic Iodochlorides: Derivatives of Phenetidine. By PAUL JANNASCH and M. NAPHTALI (*Ber.*, 1898, **31**, 1714—1716).—Phenetoil *iodochloride*, $OEt \cdot C_6H_4 \cdot ICl_2$, decomposes spontaneously in air, yielding a pale yellow oil which boils at 273—278°. By the action of chlorine, this substance is converted into chlorophenetoil *iodochloride*, which crystallises from carbon bisulphide in deep yellow prisms, and decomposes at 103°; in the dry state, it is quite stable, but rapidly decomposes when exposed to moisture, hydrogen chloride being liberated. M. O. F.

Paramidophenylic Ethylenic Ether. By WILHELM KINZEL (*Arch. Pharm.*, 1898, **236**, 260—262).—Paranitrophenylic ethylenic ether, $(NO_2 \cdot C_6H_4 \cdot O)_2C_2H_4$, prepared by the action of ethylenic dibromide on the sodium compound of paranitrophenol, crystallises from glacial acetic acid in thick, pale brown needles melting at 147°. When reduced with iron and acetic acid, it yields *paracetamidophenylic ethylenic ether* melting at 257°, which, on treatment with alcoholic hydrogen chloride, gives *paramidophenylic ethylenic ether*, $(NH_2 \cdot C_6H_4 \cdot O)_2C_2H_4$, crystallising from alcohol in long, colourless needles melting at 176°; with oxidising agents, its solutions give beautiful colour reactions. The *hydrochloride* crystallises from water in long, colourless needles melting and decomposing above 300°; the *sulphate* forms colourless needles almost insoluble in water and alcohol and decomposing above 300°; and the *oxalate* crystallises in fine, prismatic plates melting and decomposing at 285°. A. W. C.

Derivatives of Dinitro-orthocresol. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1897, [iii], **17**, 204—206).—*Potassium dinitro-orthocresol*, $C_6H_2Me(NO_2)_2 \cdot OK$ [$Me : OK : NO_2 : NO_2 = 1 : 2 : 3 : 5$], obtained on adding a slight excess of potash to a boiling aqueous solution of dinitro-orthocresol, crystallises in orange-coloured spangles soluble in water and in alcohol.

Ammonium dinitro-orthocresol, $C_6H_2Me(NO_2)_2\cdot ONH_4 + H_2O$, prepared by saturating dinitro-orthocresol with ammonia, forms golden-yellow needles soluble in water and alcohol.

Barium dinitro-orthocresol, $[C_6H_2Me(NO_2)_2\cdot O]_2Ba + 2H_2O$, is obtained in orange needles, soluble in water and alcohol, by decomposing barium carbonate with a boiling solution of dinitro-orthocresol.

Calcium dinitro-orthocresol, $[C_6H_2Me(NO_2)_2\cdot O]_2Ca + H_2O$, from calcium carbonate and dinitro-orthocresol, crystallises in fine, golden-yellow needles, soluble in water and alcohol.

Acetyldinitro-orthocresol, $C_6H_2Me(NO_2)_2\cdot OAc$, obtained by boiling acetic anhydride with dinitro-orthocresol for an hour, is a colourless compound melting at 95°, insoluble in water, but soluble in alcohol, ether, and benzene.

Nitramido-orthocresol, $C_6H_2Me(NO_2)(NH_2)\cdot OH$, is produced when dinitro-orthocresol is reduced with ammonium hydrogen sulphide. It crystallises from benzene in reddish-brown needles melting at 165°, insoluble in water, but soluble in alcohol, ether, or benzene.

Diamido-orthocresol, $C_6H_2Me(NH_2)_2\cdot OH$, formed in the reduction of dinitro-orthocresol with tin and hydrochloric acid, is an unstable substance which could not be isolated. The hydrochloride,

$$C_6H_2Me(NH_2)_2\cdot OH,2HCl,$$

crystallises in nearly colourless needles soluble in water and alcohol, insoluble in ether. N. L.

Acylation of Alcohols and Phenols in Pyridine Solution. By ALFRED EINHORN and FRIEDRICH HOLLANDT (*Annalen*, 1898, **301**, 95—115).—It has been sometimes observed that the action of benzoic chloride on polyhydric alcohols proceeds in different directions, according as pyridine or caustic soda is the medium employed. Glycerol yields the tribenzoyl derivative by both methods; the tribenzoyl derivative alone is obtained from erythritol by the Schotten-Baumann method, whilst the dibenzoyl, tribenzoyl, and tetrabenzoyl derivatives are produced in presence of pyridine. *Dibenzoylmannitol* is obtained from mannitol, using pyridine as a medium, and crystallises from alcohol in stellate aggregates of minute needles melting at 178°; it differs, therefore, from the dibenzoylmannitol described by Meunier.

The action of acidic chlorides on such phenols as eugenol, β-naphthol, pyrocatechol, resorcinol, and pyrogallol has been also studied by the authors. The *acetyl* derivative of pyrogallol crystallises in lustrous needles and melts at 171°; ferric chloride develops a brown coloration in the alcoholic solution. The *benzoyl* derivative of pyrogallol separates from chloroform in prisms and melts at 140°; the *dibenzoyl* and *tribenzoyl* derivatives melt at 108° and 89° respectively. *Ethylic pyrogalloltricarboxylate*, $C_6H_3(O\cdot COOEt)_3$, obtained by the action of ethylic chloroformate on pyrogallol dissolved in pyridine, crystallises from alcohol in small prisms melting at 58—60°; distillation resolves it into carbonic anhydride, ethylic carbonate, and the compound $C_6H_3\vdots O_3\vdots C\cdot OEt$, obtained by Bender (compare also Syniewski, Abstr., 1895, i, 602). *Ethylic pyrogalloldicarboxylate*, $OH\cdot C_6H_3(O\cdot COOEt)_2$, crystallises from water in plates and melts at 83°.

Tribenzoylgallic acid, $COOH\cdot C_6H_2(OBz)_3$, crystallises from alcohol in

small, lustrous needles, and melts at 191—192°; the *methylic* salt melts at 139°.

Methylic paracetamidosalicylate, $COOMe \cdot C_6H_3(OH) \cdot NHAc$, crystallises from alcohol in needles and melts at 147°.

When phenols are dissolved in a solution of pyridine in glacial acetic acid, treated with acetic chloride, and after an interval diluted with water, the acetyl derivative of the phenol is precipitated in quantitative amount; if benzoic chloride is substituted for acetic chloride, the same compounds are formed along with benzoic acid.

On passing carbonylic chloride into a solution of β-naphthol in glacial acetic acid containing 20 per cent. of pyridine, acetyl-β-naphthol is produced. The *propionyl* and *isobutyryl* derivatives of β-naphthol melt at 51° and 43° respectively; the *isovaleryl* derivative crystallises in long needles, and boils at 180—184° under a pressure of 20 mm.

Formyleugenol is a colourless oil having the odour of eugenol; it boils at 150° under a pressure of 20 mm. The *formyl* derivative of isoeugenol boils at 155—160° under a pressure of 20 mm.; both compounds yield formylphenylhydrazine when treated with aqueous phenylhydrazine hydrochloride and sodium acetate.

Orthocresol carbonate, $CO(O \cdot C_6H_4Me)_2$, crystallises from alcohol in silky needles and melts at 60°. *β-Naphthylic carbonate*, $CO(O \cdot C_{10}H_7)_2$, crystallises from toluene in lustrous leaflets and melts at 178°.

M. O. F.

Methylphloroglucinol. By HUGO WEIDEL (*Monatsh.*, 1898, **19**, 223—235. Compare this vol., i., 304).—*Methylphloroglucinol* is obtained as a brown, friable, crystalline mass when an aqueous solution of 2 : 4 : 6-triamidotoluene hydrochloride, heated for 30 hours with water free from oxygen, is extracted with amylic alcohol, the extract subjected to steam distillation, and the residual solution evaporated under reduced pressure. When pure, it crystallises on adding xylene to its solution in ethylic acetate in white needles which darken at 170—180°, and melt at 214—216°; it is soluble in water, alcohol, ether, ethylic acetate, and hot glacial acetic acid, but only slightly so in boiling xylene, and insoluble in benzene and light petroleum.

Methylphloroglucinol reduces ammoniacal silver nitrate in the cold, and produces violet colorations with ferric chloride and with a pine shaving moistened with hydrochloric acid; it is sweet with a bitter after-taste, and, like phloroglucinol, it reacts both as a tribydric phenol and also as a ketone.

Triacetylmethylphloroglucinol, obtained by heating methylphloroglucinol with acetic anhydride, forms an opaque, white mass of microscopic needles; it melts at 52°, dissolves readily in alcohol, ethylic acetate, benzene, and light petroleum, but is only slightly soluble in hot water.

Ethylic methylphloroglucinol carbonate, $C_6H_2Me(O \cdot COOEt)_3$, separates as a heavy oil when ethylic chlorocarbonate is added to a cooled solution of methylphloroglucinol in caustic soda; it boils without decomposition at 245°—248° under a pressure of 17 mm. and does not solidify at 20°.

Methylphloroglucinol methylic ether, $C_6H_2Me(OH)_2\cdot OMe$, is prepared by saturating a cold solution of methylphloroglucinol in absolute methylic alcohol with hydrogen chloride, dissolving the crystalline precipitate which forms in benzene, evaporating the solution to dryness, and distilling the residue under reduced pressure. It crystallises from xylene in lustrous, colourless needles, melts at 124°, and boils at 195—198° under a pressure of 20 mm. It dissolves easily in alcohol and ethylic acetate, but only slightly in water and light petroleum; its aqueous solution gives no colour reactions with ferric chloride or with a pine shaving moistened with hydrochloric acid.

Methylphloroglucinol dimethylic ether, $C_6H_2Me(OMe)_2\cdot OH$, is produced together with some monomethylic ether when the above experiment is performed on a warm solution. By crystallisation from benzene, the monomethylic ether can be separated in the crystalline state, and the mother liquor, when evaporated and distilled, yields a pasty mass from which the dimethylic ether can be separated by crystallisation from xylene as a flocculent mass of small needles; it boils at 178—180° under 20 mm. and melts at 60—61°; it is very soluble in alcohol, ether, ethylic acetate, benzene, and xylene, but almost insoluble in petroleum and hot water.

Two monomethylic and two dimethylic ethers are theoretically possible, and the author has not yet determined the position of the methoxyl groups in the ethers described.

Methylphloroglucinol reacts with hydroxylamine, but the product has not been identified. G. T. M.

2 : 4-Dimethylphloroglucinol. By HUGO WEIDEL and FRANZ WENZEL (*Monatsh.*, 1898, **19**, 236—246).—2 : 4-*Dimethylphloroglucinol*, prepared from the hydrochloride of 2 : 4 : 6-triamidometaxylene by the method employed in the production of methylphloroglucinol (compare previous abstract) crystallises from xylene in pale yellowish-white needles, and melts at 163°; it is soluble in water and the usual organic solvents. When precipitated by xylene from its solution in glacial acetic acid, it contains acetic acid of crystallisation, but if the solution, placed over lime, is allowed to evaporate in a vacuum, monoclinic prisms are obtained which are free from this solvent. An aqueous solution deposits monoclinic prisms containing $3H_2O$. Dimethylphloroglucinol, like its homologues, gives characteristic colour reactions with ferric chloride and the pine shaving, and reduces ammoniacal silver nitrate in the cold; its aqueous solution is acid to phenolphthalein, and one molecular proportion of soda is required to produce neutrality.

Triacetyldimethylphloroglucinol crystallises from ethylic acetate in aggregates of lustrous needles and melts at 123°; it dissolves with difficulty in ether, but is readily soluble in alcohol.

Ethylic dimethylphloroglucinol dicarbonate, $OH\cdot C_6HMe_2(O\cdot COOEt)_2$, obtained, like the corresponding compound, from methylphloroglucinol, is a transparent oil which solidifies on standing, but liquefies on warming to 35—40°, and boils at 242—243° under a pressure of 16 mm. It dissolves in ether and alcohol in all proportions, but is less soluble in benzene and petroleum; from all these solvents, it separates as an oil.

Dimethylphloroglucinol methylic ether, $C_6HMe_2(OH)_2 \cdot OMe$, prepared like the corresponding derivative of methylphloroglucinol, boils at 188° under 21 mm. pressure, and crystallises from benzene in aggregates of colourless leaflets; it melts at 100—101°. This methyl derivative is readily soluble in alcohol, less soluble in water, and gives no colour reactions with ferric chloride or the pine shaving.

During the conversion of triamidometaxylene into dimethylphloroglucinol, a bye-product is obtained which is insoluble in ether and is extracted from the aqueous solution by amylic alcohol; it has the composition $C_6HMe_2(OH)_2 \cdot NH_2,HCl$, and is probably formed from a triamidometaxylene other than the 2 : 4 : 6-compound. In the preparation of 2 : 4 : 6-trinitrometaxylene, small quantities of the other two isomerides are formed, and these, on reduction, would give rise to triamidometaxylenes which might not part with all their amidogen groups on boiling with water. G. T. M.

2 : 4 : 6-Triamidotrimethylbenzene and Trimethylphloroglucinol. By HUGO WEIDEL and FRANZ WENZEL (*Monatsh.*, 1898, 19, 249—267).—The *hydrochloride* of *triamido*-1 : 3 : 5-*trimethylbenzene*, obtained by the reduction of trinitromesitylene with tin and hydrochloric acid, crystallises in small, colourless leaflets which are very insoluble in alcohol and in concentrated hydrochloric acid; when heated, the salt decomposes without melting. The free *base* crystallises from xylene in small, pale yellow needles which darken on exposure to the air; it melts at 117—119°, dissolves readily in hot water, but is only slightly soluble in benzene, light petroleum, ether, and ethylic acetate. When heated with excess of acetic anhydride, triamidotrimethylbenzene is converted into *triacetyldiamidohydroxytrimethylbenzene* $C_6Me_3(NHAc)_2 \cdot OAc$, which crystallises from xylene in clusters of needles melting at 204—205°; an alcoholic solution slightly diluted with water yields the substance in glistening prisms.

2 : 4 : 6-*Diamidohydroxytrimethylbenzene hydrochloride*, obtained by hydrolysing the preceding compound, crystallises from dilute hydrochloric acid in glistening needles. On long boiling with water, both the above-mentioned hydrochlorides yield trimethylphloroglucinol; this substance crystallises from glacial acetic acid or xylene in colourless needles having a silky lustre, melts at 150°, and is identical with the compound formerly obtained by O. Margulies (compare Abstr., 1889, 1153). When crystallised from an aqueous solution, it contains $3H_2O$. Trimethylphloroglucinol has a slightly bitter taste, reduces ammoniacal silver nitrate, and gives a transient colour reaction with ferric chloride, but none with the pine shaving; it is readily soluble in methylic and ethylic alcohols and ethylic acetate, and slightly in hot benzene and petroleum.

Triacetyltrimethylphloroglucinol crystallises from benzene in short, monoclinic prisms melting at 102°; it is soluble in alcohol, ether, and ethylic acetate.

Ethylic trimethylphloroglucinol dicarbonate $OH \cdot C_6Me_3(O \cdot COOEt)_2$, is a colourless, viscid, uncrystallisable mass boiling at 230—232° under a pressure of 14 mm. As in the case of dimethylphloroglucinol, only the dicarboxylate is obtained, even with excess of ethylic chlorocarbonate.

Trimethylphloroglucinol methylic ether, $C_6Me_3(OH)_2 \cdot OMe$, crystallises from benzene in colourless needles readily soluble in alcohol, ethylic acetate, and hot water; it melts at 120—121° and boils at 196—198° under 20 mm. pressure. G. T. M.

Paramidobenzaldehyde. By REINHOLD WALTHER and WILHELM BRETSCHNEIDER (*J. pr. Chem.*, 1898, [ii], **57**, 535—539).—Kalle & Co., of Biebrich, have patented a method (D.R.-P. No. 89244) for the preparation of nitroparamidobenzaldehyde. No mention is made in the patent of the position of the nitro-group, but as the substance is a mono-substitution product of a para-compound, the nitro-group can only occupy the ortho- or meta-position relatively to the aldehydic group. The production of such compounds would be of great interest for the synthesis of members of the indigo group and certain dioxy-compounds.

Although the authors worked exactly according to the instructions given in the patent, they were unable to obtain a mononitro-derivative but only a *dinitramidobenzaldehyde* melting at 168°, whereas the melting point of the supposed mononitro-derivative is given at 170°. Further investigation of the substance was therefore abandoned.

The following affords a cheap means of preparing parahydroxybenzaldehyde. To a hot solution of paramidobenzaldehyde in hydrochloric acid, sodium nitrite is added, and when the reaction is ended the whole is filtered and the filtrate decomposed with sodium hydrogen suphite, and evaporated to one-third of its volume. On cooling, parahydroxybenzaldehyde separates in silken crystals melting at 115—116°.

When a solution of the hydrochloride of paramidobenzaldehyde is treated with sodium nitrite in presence of nitric acid, *mononitroparahydroxybenzaldehyde* is obtained in good yield as yellow needles melting at 131—133°. Attempts to prepare an oxy-indigo by Baeyer's reaction by means of acetone and caustic soda failed, and therefore the substance has probably the constitution $C_6H_3(COH)(NO_2) \cdot OH$ [= 1 : 3 : 4]. A. W. C.

Synthesis of Aromatic Hydroxyaldehydes. By LUDWIG GATTERMANN and W. BERCHELMANN (*Ber.*, 1898, **31**, 1765—1769. Compare this vol., i, 476).—The Friedel-Crafts reaction is not only applicable to phenolic ethers in the manner already described (*loc. cit.*), but may be employed in the preparation of aromatic hydroxyaldehydes from phenols, these being gently heated with hydrogen cyanide, benzene, and aluminium chloride, while a current of hydrogen chloride is passed through the liquid. The yield in many cases is almost quantitative.

1 : 4-*Hydroxynaphthaldehyde*, $OH \cdot C_{10}H_6 \cdot COH$, crystallises from dilute alcohol in pale yellow needles and melts at 181°.

1 : 2 : 3 : 4-*Trihydroxybenzaldehyde*, $(OH)_3C_6H_2 \cdot COH$, prepared by this means from pyrogallol, crystallises from water in colourless needles, and melts at 157—158°. M. O. F.

Tetramethyldiamidobenzophenone Derivatives. By EDOUARD GRIMAUX (*Compt. rend.*, 1898, **126**, 1117—1118).—The dinitro-compound, $CO(NO_2 \cdot C_6H_3 \cdot NMe_2)_2$, obtained by the action of potassium

nitrate on the ketone in presence of concentrated sulphuric acid, forms small, orange crystals which melt at 165—166°. It is probably a meta-derivative. The amido-derivative does not crystallise.

The dibromo-derivative, $CO(C_6H_3Br\cdot NMe_2)_2$, forms hard, brilliant prisms which melt at 130—131°.

Both these compounds interact with dimethylaniline and phenyl-α-naphthylamine in presence of phosphorus chlorides, yielding colouring matters which are less brilliant than those obtained with the parent substance, so that the introduction of the bromine or the nitro-group has no advantages. C. H. B.

Reduction of Methylcyclohexenone. By CARL D. HARRIES (*Ber.*, 1898, **31**, 1806—1807. Compare Knoevenagel and Tübben, Abstr., 1897, i, 607).—*Diketodimethyldihexahydrophenyl*, $C_{14}H_{22}O_2$, is obtained by reducing methylcyclohexenone with alcohol and sodium amalgam in a freezing mixture; it separates from ether in slender, white needles, and melts at 160—161°. The *hydrazone* melts at 210°.
M. O. F.

Condensation of Salicylaldehyde with Acidic Amides. By FRANZ CEBRIAN (*Ber.*, 1898, **30**, 1592—1604).—Under the influence of anhydrous sodium acetate, salicylaldehyde yields condensation products with acidic amides, combining with these substances in molecular proportion. The compounds obtained from this source have a constitution expressed by the general formula $C_6H_4<\begin{matrix}O—CR\cdot OH\\ CH:N\end{matrix}$, in which R represents the radicle which characterises the original amide; to substances of this type, the author gives the name *coumarazine*, in order to indicate their relation to coumarin, $C_6H_4<\begin{matrix}O—CO\\ CH:CH\end{matrix}$. The coumarazines are yellow compounds, and develop a beautiful red coloration with concentrated sulphuric acid; oxidation with potassium permanganate converts them into *coumarazone*, $C_6H_4<\begin{matrix}O—CO\\ CH:N\end{matrix}$, which is easily hydrolysed.

Methylhydroxycoumarazine, $C_6H_4<\begin{matrix}O—CMe\cdot OH\\ CH:N\end{matrix}$, is obtained by heating an intimate mixture of acetamide (5 grams), anhydrous sodium acetate (6 grams), and salicylaldehyde (10 grams) in an oil bath at 130—140° for 2—3 hours; when water vapour is no longer set free, the product is left in contact with water (200 c.c.) during 12 hours, when it is powdered and filtered. The product, which is lemon yellow, is practically insoluble in common agents; above 150°, it gradually decomposes and becomes brown. It is insoluble in alkali carbonates, but caustic alkalis form yellow solutions which exhibit feeble reddish-violet fluorescence. If the substance is obtained by adding dilute acetic acid to a solution in alkali, it dissolves appreciably in both alcohol and acetic acid if treated with these agents while still moist. A solution in alkali, which has been exactly neutralised with dilute acetic acid, yields a white precipitate with silver nitrate, but this turns black almost immediately; lead acetate and mercuric chloride produce

yellow precipitates which become brown, whilst copper sulphate yields a greenish-white precipitate, which rapidly alters in appearance. The *barium* derivative, which is yellow, separates on adding absolute alcohol to the aqueous solution; it contains $1H_2O$, and becomes deep brown when exposed to light and air. The *acetyl* derivative, which is a snow-white powder melting at 263—264°, dissolves in alcohol, chloroform, and glacial acetic acid, and is hydrolysed by cold alkali. The *benzoyl* derivative is a white, amorphous powder, which melts and decomposes at 191°; it dissolves in alcohol, acetic acid, and chloroform, but is insoluble in ether. The *benzylic* and *ethylic* ethers decompose at 185° and 235—240°, without previously undergoing fusion. The *nitro*-derivative, a pale-yellow, amorphous powder, dissolves in alcohol, glacial acetic acid, alkalis, and alkali carbonates; it decomposes at 75°. The *nitro*-derivative of methylacetoxycoumarazine, obtained by the action of acetic anhydride on the foregoing substance, melts and decomposes at 131°.

Coumarazone, $C_6H_4<\begin{matrix}O—CO\\CH:N\end{matrix}$, prepared by oxidising methylhydroxycoumarazine in 15 per cent. sulphuric acid with potassium permanganate, crystallises from glacial acetic acid, and decomposes above 70°. Hydrolysis with alkalis converts it into orthohydroxybenzylideneamidoformic acid, $OH\cdot C_6H_4\cdot CH:N\cdot COOH$, the *barium* salt of which crystallises with $3H_2O$, and is decomposed by light.

Methylhydroxycoumarazine is not easily resolved into its components. When heated with concentrated caustic potash at 150° during 5 hours, it yields ammonia, acetic acid, and the anhydride of salicylaldehyde, $C_{14}H_{10}O_3$; fusion with potash eliminates ammonia, and gives rise to salicylic acid.

Hydroxycoumarazine, $C_6H_4<\begin{matrix}O—CH\cdot OH\\CH:N\end{matrix}$, obtained from salicylaldehyde and formamide, is a yellow, amorphous powder readily soluble in alcohol and glacial acetic acid, and melts at 98°. The *acetyl* derivative melts at 203°, and the *ethylic* ether decomposes at 210° without previous fusion. Oxidation converts hydroxycoumarazine into coumarazone.

Phenylhydroxycoumarazine, $C_6H_4<\begin{matrix}O—CPh\cdot OH\\CH:N\end{matrix}$, which is a yellow, insoluble, amorphous powder, dissolves in alkalis, but is insoluble in alkali carbonates. The *acetyl* derivative melts at 211—212°, and dissolves readily in glacial acetic acid, chloroform, and ethylic acetate; the *ethylic* ether decomposes at 200°, but does not melt. Hydrolysis with concentrated alkali eliminates ammonia and benzoic acid from phenylhydroxycoumarazine. M. O. F.

Synthesis of Flavone. By W. Feuerstein and Stanislaus von Kostanecki (*Ber.*, 1898, 31, 1757—1762. Compare this vol., i, 369).—On the lines followed in recent syntheses of flavone derivatives (*loc. cit.*), the authors have obtained the parent substance from the acetyl derivative of 2′-hydroxybenzylideneacetophenone (this vol., i, 371).

2′-Acetoxybenzylideneacetophenone, $OAc\cdot C_6H_4\cdot CO\cdot CH:CHPh$, crystal-

lises from dilute alcohol in small, pale yellow plates, and melts at 51—52°; the *dibromide* melts at 105—107°.

Flavone, $C_6H_4<\begin{matrix}O—CPh\\CO\cdot\overset{\|}{C}H\end{matrix}$, obtained by the action of alcoholic potash on the dibromide of 2′-acetoxybenzylideneacetophenone, crystallises from petroleum in aggregates of white needles melting at 97°. The solution in concentrated sulphuric acid is yellow, and exhibits very feeble blue fluorescence. The compound described by Friedländer and Neudörfer under the name flavone (Abstr., 1897, i, 425) is *benzylidenecoumaranone*, $C_6H_4<\begin{matrix}O\\CO\end{matrix}>C\colon CHPh$. Fusion with potash resolves flavone into salicylic acid and acetophenone on the one hand, orthohydroxyacetophenone and benzoic acid being produced at the same time (compare Abstr., 1894, i, 93). The two last-named substances are the sole products of hydrolysis with sodium ethoxide. M. O. F.

Isomeric Chlorides of Orthosulphobenzoic Acid: A Case of Tautomerism. By REINHOLD LIST and MAX STEIN (*Ber.*, 1898, 31, 1648—1672).—The crude chloride obtained by acting on orthosulphobenzoates with phosphorus pentachloride at ordinary temperatures is a mixture of two isomeric chlorides, which melt at 79° and 40°, and are produced in the proportion represented by 30—40 per cent. and 60—70 per cent. respectively (compare Remsen, Abstr., 1895, i, 472). Both chlorides are capable of action in accordance with the alternative formulæ, $COCl\cdot C_6H_4\cdot SO_2Cl$ and $C_6H_4<\begin{matrix}CCl_2\\SO_2\end{matrix}>O$, representation by rigid formulæ, and employment of the terms symmetrical and unsymmetrical, being, therefore, inadmissible. The substance melting at 79°, however, enters much more slowly into action than the isomeride; it is consequently referred to as the stable chloride, the compound which melts at 40° being called the labile chloride.

The stable chloride is prepared from the crude mixture by agitating the ethereal solution with ammonia, which attacks it very slowly, yielding orthobenzoicsulphinide; whereas the labile compound is rapidly decomposed, becoming converted chiefly into orthocyanobenzenesulphonic acid. In order to obtain the chloride of lower melting point, the mixture is distilled under reduced pressure, the stable compound being resolved into sulphurous anhydride and orthochlorobenzoic chloride. The labile substance is also the sole product when normal potassium sulphobenzoate is heated with phosphorus oxychloride at 130°. The stable chloride crystallises in the monoclinic system; $a:b:c = 1{\cdot}8521:1:2{\cdot}0057$. $\beta = 89°\ 28'$. The labile compound is rhombic; $a:b:c = 1{\cdot}8103:1:2{\cdot}0997$. In optical characteristics, the two substances closely resemble each other. Water converts them both into orthosulphobenzoic and hydrochloric acids.

Aniline has the same action on both chlorides, yielding the symmetrical anilide, $NHPh\cdot CO\cdot C_6H_4\cdot SO_2\cdot NHPh$, sulphobenzanilide, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NPh$, and the unsymmetrical anilide,

$$C_6H_4<\begin{matrix}C(NHPh)_2\\SO_2\end{matrix}>O,$$

Alcohol converts the two chlorides into ethylic sulphobenzoate, $COOEt \cdot C_6H_4 \cdot SO_3H$, the chloride of this acid being the initial product in the case of the labile substance. Phenol also has the same action on both, yielding the sulphochloride of phenylic benzoate,

$$COOPh \cdot C_6H_4 \cdot SO_2Cl,$$

and diphenylic sulphobenzoate, $COOPh \cdot C_6H_4 \cdot SO_3Ph$; the latter is also formed when benzene condenses with the chlorides under the influence of aluminium chloride.

Sulphobenzide is the name given by the authors to the compound, $C_6H_4 < \begin{smallmatrix} CH_2 \\ SO_2 \end{smallmatrix} > O$, obtained by reducing the stable chloride (compare Jones, Abstr., 1894, i, 417); it crystallises from alcohol in leaflets, and melts at 112—113°. Prolonged treatment with boiling water converts it into hydroxymethylbenzenesulphonic acid; the *barium* salt crystallises in needles and contains $1H_2O$, whilst the *copper* salt, which is light blue, contains $2H_2O$. The *silver* salt forms needles.

The labile chloride, which yields thiosalicylic acid, $SH \cdot C_6H_4 \cdot COOH$, on reduction, softens at 158°, and melts at 163—164°. Dithiosalicylic acid is readily obtained from thiosalicylic acid on oxidation.

M. O. F.

Fluorescence of Anthranilic Acid. By BRONISLAW PAWLEWSKI (*Ber.*, 1898, **31**, 1693).—It has long been on record that aqueous solutions of anthranilic acid exhibit feeble blue fluorescence. The author has observed that solutions in alcohols, fatty acids, ketones, and ethereal salts exhibit the phenomenon distinctly, a marked violet shade being noticeable when ether, benzene, chloroform, bromobenzene, epichlorhydrin, ethylic carbonate, ethylic chloracetate, and anisoil are employed. Anthranilic acid dissolved in an aqueous solution of formaldehyde gives a powerful, dark blue fluorescence, which is undiminished after exposure to light during many weeks. Solutions in œnanthaldehyde, oleic acid, and glycerol exhibit beautiful fluorescence, but no such effect is produced with carbon bisulphide, carbon tetrachloride, chloropicrin, formic acid, or phenylic isocyanide.

M. O. F.

Aromatic Glyoxylic Acids. By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], **17**, 363—366. Compare Abstr., 1897, i, 530).—Some improvements have been effected in the preparation of the glyoxylic acids, which are obtained by the interaction of aromatic hydrocarbons and ethylic chloroglyoxylate in presence of aluminium chloride (*loc. cit.*). It is found that the addition of nitrobenzene, in the proportion of one and a half times the weight of aluminium chloride employed, renders the action more regular, and prevents the formation of insoluble products. The alkali salts resulting from the hydrolysis of the ethereal glyoxylates are decomposed by hydrochloric acid, and the liquid shaken with ether; the residue left on evaporating the ether is dried at 100°, and the acid purified by crystallisation from hot carbon bisulphide. The glyoxylic acids are strong acids, not displaced by acetic acid; a property useful in effecting their separation from small quantities of aromatic acids, products of their decomposition, with which they are sometimes contaminated.

Attempts were made to prepare the amylic salts of various glyoxylic acids, the ethylic chloroglyoxylate being replaced by amylic chloroglyoxylate. Amylic anisoilglyoxylate and veratroleglyoxylate were readily obtained, but amylic phenylglyoxylate could not be prepared, decomposition taking place immediately, with formation of benzene and amylic chloride. Ethylic cymylglyoxylate is also unstable, and undergoes decomposition into cymene and ethylic chloride, which then interact to form ethylcymene.

The decomposition by heat of the glyoxylic acids, R·CO·COOH, takes place in two ways, with formation of aldehydes, R·CHO, and acids, R·COOH. The second reaction, it is now found, can be exclusively brought about by heating the acids with concentrated sulphuric acid and pouring the cooled liquid into water. The same decomposition is effected by phosphorus trichloride and oxychloride, as was discovered in attempts to prepare glyoxylic acid chlorides. N. L.

Some New γ-Ketonic Acids. By TIMOTHÉE KLOBB (*Bull. Soc. Chim.*, 1897, [iii], 17, 408—411).—The ethereal salts of the alkylphenacylcyanacetic acids, C_6H_5·CO·CH_2·CR(CN)·COOH, undergo ordinary hydrolysis in the cold, but when warmed with alkalis, γ-ketonic acids, C_6H_5·CO·CH_2·CHR·COOH, are produced, with elimination of ammonia and carbonic anhydride. The following acids were prepared in this way.

Phenacylmethylacetic acid, C_6H_5·CO·CH_2·CHMe·COOH, obtained by heating methylic phenacylmethylcyanacetate with the theoretical quantity of alcoholic sodium hydroxide and extracting the acidified liquid with ether, crystallises in colourless needles melting at 136°. It is insoluble in water, but soluble in most organic solvents. The *potassium* salt crystallises well, and is very soluble in water.

Phenacylethylacetic acid, C_6H_5·CO·CH_2·CHEt·COOH, from ethylic phenacylethylcyanacetate, forms colourless needles melting at 83°, and is no doubt identical with the acid obtained by Dittrich and Paal by the decomposition of β-benzoyl-α-ethylisosuccinic acid, and stated by them to melt at 81—83°.

Phenacylpropylacetic acid, C_6H_5·CO·CH_2·CHPr·COOH, crystallises in colourless needles melting at 56°. For the preparation of this acid, two hitherto undescribed ethereal salts were prepared: *methylic phenacylpropylcyanacetate* melting at 88°, and the corresponding *ethylic* salt melting at 48—49°.

Benzylphenacylacetic acid, C_6H_5·CO·CH_2·CH(C_7H_7)·COOH, from ethylic benzylphenacylcyanacetate, crystallises in short, colourless prisms melting at 170°. It is insoluble in water, but more or less soluble in most organic solvents. N. L.

Caffeine Compound in Kola. Part II. Kolatannin. By JAMES W. T. KNOX and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1898, 20, 34—78. Compare this vol., i, 278).—The authors find that the tannin of the caffeine kolatannate, although not quite as light coloured as the free tannin contained in the nuts, is identical with it. The latter was obtained as follows. The sliced nuts were immersed in boiling alcohol for a few minutes, dried, ground to powder, and extracted with 50 per cent. alcohol. The alcoholic extract, concentrated in a vacuum at 18—20°, was filtered from the insoluble caffeine kolatannate and

colouring matter, the rest being precipitated by adding sodium chloride; the filtrate was washed with chloroform to remove fat and alkaloids, then with ether, and finally the tannin was extracted with ethylic acetate. After purifying, the kolatannin, $C_{16}H_{20}O_8$, was obtained as a cream coloured powder easily soluble in water, acetone, and alcohol, sparingly so in ether, and insoluble in chloroform and light petroleum. Its reactions closely resemble those of oak tannin. The pentacetyl derivative is a nearly white, tasteless powder, insoluble in water, sparingly soluble in ether, and easily in chloroform, alcohol, and glacial acetic acid. By the action of bromine water on an aqueous solution of the tannin, a reddish-brown, odourless, and almost tasteless tribromo-derivative is obtained, insoluble in water, ether, chloroform, and benzene, but easily soluble in alcohol and acetone.

Pentacetyltribromokolatannin, $C_{16}H_{12}Br_3(C_2H_3O)_5O_8$, prepared from the tribromo-tannin or the pentacetyl-tannin, is a tasteless, golden-yellow powder with a faint odour of acetic acid; when gently heated, it loses acetic acid, and both bromine and acetic acid on heating more strongly. A tetrabromo-derivative of the tannin, prepared by the action of bromine on an alcoholic solution of the tannin, resembles the tribromo-derivative, but is slightly darker and has a faint odour of bromine. The pentacetyltetrabromo-derivative is slightly darker than the corresponding tribromo-derivative, but otherwise closely resembles it. A pentabromo-derivative of the tannin was also obtained; it is less stable than the tetrabromo-derivative, has a stronger odour of bromine, and yields a pentacetyl derivative. By the action of a considerable excess of bromine on an alcoholic solution of the tannin, a hexabromo-derivative was prepared; this is darker in colour than the other bromo-derivatives, has a stronger odour of bromine, and yields a tetracetyl derivative. By heating the tannin at 107—110°, 135—140°, and 155—160°, the anhydrides $(C_{16}H_{19}O_7)_2O$, $(C_{16}H_{17}O_6)_2O$, and $C_{16}H_{16}O_6$ are formed respectively. The first is darker coloured than the tannin itself, and less soluble in water; the second is dark reddish-brown and insoluble in water, and the last is dark brown and insoluble in water. All the anhydrides are soluble in alcohol and in a concentrated solution of the tannin. According to the authors, an anhydride, $C_{16}H_{18}O_7$, could also probably be obtained by heating the tannin at 120—125°. Bromine derivatives of the various anhydrides are also described.

When kolatannin is boiled with dilute sulphuric or hydrochloric acid, a red or dark brown, amorphous substance is formed which, according to the authors, is probably a decomposition product and not an anhydride.

Further experiments have failed to confirm the formation of glucose when the tannin is hydrolysed, and hence the tannin is not a glucoside, as at first supposed. When the tannin is fused with potassium hydroxide, protocatechuic acid and phloroglucinol are formed, and the former acid is also obtained by heating the tannin with glycerol at 195—200°. The tannin obtained from caffeine kolatannate was found to yield the same derivatives, and to undergo the same reactions as the uncombined tannin.

Criticisms of the methods of Jean (*Rep. de Pharm.*, 1896, [iii], 7,

49) and of Carles (*J. Pharm. Chim.*, **16**, 104) for the assay of kola are appended. E. W. W.

Action of Nitric Acid at the Ordinary Temperature on Certain Aromatic Amides. By H. J. TAVERNE (*Rec. Trav. Chim.*, 1898, **17**, 190—196. Compare Abstr., 1897, i, 619).—Although the mono- and di-methylamides of benzoic, phenylacetic, and phenylpropionic acids, when treated for a short time at 0° with nitric acid, yield nitrated derivatives containing the nitro-group in the nucleus, yet with nitric acid at the ordinary temperature a very different reaction takes place, and the amides become decomposed in much the same manner as described by Franchimont for the aliphatic amides.

Benzamide, phenylacetamide, and phenylpropionamide yield nitrous oxide, as also do metanitrobenzamide, paranitrophenylacetamide, and paranitrophenylpropionamide. The corresponding monomethylamides yield both nitrous oxide and methylic nitrate, and the dimethylamides yield dimethylnitramine. At the same time, the acids thus formed become nitrated, but not in the same manner as at a lower temperature.

The amides of benzoic acid yield both meta- and ortho-nitrobenzoic acid; metanitrobenzamide and its mono- and di-methyl derivatives yield metanitrobenzoic acid, but no dinitro-acids. The amides of phenylacetic and paranitrophenylacetic acids yield 2 : 4-dinitrophenylacetic acid melting at 160°; this acid, if heated above its melting point, or if boiled with barium hydroxide solution, loses carbonic anhydride and yields 1 : 2 : 4-dinitrotoluene [$Me : (NO_2)_2 = 1 : 2 : 4$]. The amides of phenylpropionic acid and of its paranitro-derivative yield 2 : 4-dinitrophenylpropionic acid (compare Abstr., 1879, 639). J. J. S.

Action of Phenylcarbimide on some Alkyloxy-acids. By EUGÈNE LAMBLING (*Bull. Soc. Chim.*, 1897, [iii], **17**, 356—362).—The reaction between phenylcarbimide and certain organic acids has been found by Haller to take place in two stages, with formation of (1) anhydrides of the acids and diphenylcarbamide, which then interact to form (2) anilides, with elimination of carbonic anhydride. The author has studied the action of phenylcarbimide on methoxy-, ethoxy-, phenoxy-, thymoxy-, and eugenoxy-acetic acids, α-phenoxypropionic acid, and benzoyllactic acid, but finds that, whether the reaction occurs slowly and partially at a low temperature or quickly at a high temperature, anilides are the sole product. Phenoxyacetanilide, from phenoxyacetic acid and phenylcarbimide, has been previously obtained by Fritsche, but the following anilides have not yet been described; they have all been identified with the products of the direct action of aniline on the acids.

Methoxyacetanilide, $OMe\cdot CH_2\cdot CO\cdot NHPh$, crystallises from light petroleum in colourless needles melting at 58°, and boiling at 185—188° under 40 mm. pressure; it is soluble in hot water, alcohol, ether, and chloroform.

Ethoxyacetanilide, $OEt\cdot CH_2\cdot CO\cdot NHPh$, is a yellowish oil boiling at about 185° under a pressure of 35 mm.

Thymoxyacetanilide, $C_{10}H_{13}\cdot O\cdot CH_2\cdot CO\cdot NHPh$, forms colourless needles melting at 81°, insoluble in water, but soluble in ether, alcohol, and light petroleum.

Eugenoxyacetanilide, $C_3H_5 \cdot C_6H_3(OMe) \cdot O \cdot CH_2 \cdot CO \cdot NHPh$, separates from light petroleum in almost colourless, prismatic crystals melting at 54°.

a-Phenoxypropionanilide, OPh·CHMe·CO·NHPh, crystallises from light petroleum in light scales melting at 117°.

Benzoyllactanilide, OBz·CHMe·CO·NHPh, crystallises from boiling alcohol in colourless needles melting at 153°. N. L.

Action of a Solution of Hydrogen Chloride in Methylic Alcohol on the Phenylimides of Dibasic Acids. By SEBASTIAAN HOOGEWERFF and WILLEM ARNE VAN DORP (*Rec. Trav. Chim.*, 1898, **17**, 197—201).—Maleinanil (Abstr., 1887, 934), when boiled with methylic alcohol containing hydrogen chloride in solution, combines with the alcohol, yielding *methylic maleinphenylamate*,

COOMe·CH:CH·CO·NHPh.

It is best obtained by dissolving maleinanil (4 grams) in absolute methylic alcohol (28 grams), adding 4 grams of methylic alcohol saturated with dry hydrogen chloride, and boiling; at the end of a few minutes, another 4 grams of the saturated solution of hydrogen chloride is added, and the mixture again boiled until it weighs 24 grams. Recrystallised from benzene, it forms colourless plates melting at 77—79°, and decomposing at 145—150°. It dissolves very readily in alcohol, acetone, and ether, fairly readily in benzene, but only sparingly in light petroleum. Boiling water transforms it first into maleinanil and then into phenylasparaginanil (Anschütz and Wirtz, Abstr., 1887, 934).

Succinanil behaves in much the same way, yielding *methylic succinophenylamate*, $COOMe \cdot CH_2 \cdot CH_2 \cdot CO \cdot NHPh$, which, when precipitated from its alcoholic solution by water, forms colourless needles melting at 97—99° (Meulen, Abstr., 1897, i, 415).

Methylic chlorosuccinophenylamate, obtained from monochlorosuccinanil, crystallises from benzene in colourless needles and plates melting at 101—103°.

Succinimide, succinobenzylimide, camphorimide, phthalimide, and phthalanil are not acted on when boiled with methylic alcohol containing hydrogen chloride. J. J. S.

Comparison of Imido-ethers with the Rosanilines. A Reply to Miolati. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1897, [iii], **17**, 373—376).—From a minute consideration of the reactions of imidoethers and the rosanilines, the author shows that the analogy between these two classes of compounds, which has been suggested by Miolati, does not hold good. N. L.

Synthesis of Indigo Colouring Matters. By RUBIN BLANK (*Ber.*, 1898, **31**, 1812—1817).—When ethylic anilidomalonate is heated, ethylic alcohol is eliminated, with production of indoxylic acid. This reaction is a general one, and affords a means of producing higher homologues of indigo.

Ethylic anilidomalonate, $NHPh \cdot CH(COOEt)_2$, obtained by the action of aniline (2 mols.) on ethylic bromomalonate, crystallises from alcohol, and melts at 45°. *Ethylic paratoluidomalonate* and *ethylic β-naphthylamidomalonate* melt at 55° and 88° respectively.

Ethylic paratolylindoxylate, $C_6H_3Me<\substack{NH\\CO}>CH\cdot COOEt$, prepared by heating ethylic paratoluidomalonate at 250—255°, melts at 155—156°; its solution in concentrated sulphuric acid is pale yellow, and becomes greenish-blue when heated, owing to the formation of paratolylindigosulphonic acid. *Paratolylindigo* is produced by hydrolysing ethylic paratolylindoxylate with boiling alkali, and passing air through the solution; it resembles ordinary indigo, but dissolves more readily.

Ethylic β-naphthylindoxylate melts at 158°; hydrolysis followed by oxidation converts it into β-naphthylindigo (Wichelhaus, Abstr., 1894, i, 42). M. O. F.

Dimethoxydiphenyl. By PAUL JANNASCH and E. KÖLITZ (*Ber.*, 1898, 31, 1745—1746).—*Dimethoxydiphenyl*, $OMe\cdot C_6H_4\cdot C_6H_4\cdot OMe$, is prepared by heating orthoiodanisoil, dissolved in xylene, with sodium wire, after the liquid has remained in contact with the metal for 12 hours. It crystallises from alcohol in long, white prisms, melts at 155°, and boils at 299·5—301°. M. O. F.

The Phthalein Group. By RICHARD MEYER and LEO FRIEDLAND (*Ber.*, 1898, 31, 1739—1744. Compare Abstr., 1892, 1228).—2 : 7 *Dinitrofluoran*, $\begin{matrix}CO\cdot O\\ | \\ C_6H_4\end{matrix}>C<\begin{matrix}C_6H_3(NO_2)\\C_6H_3(NO_2)\end{matrix}>O$, obtained by the action of nitric acid of sp. gr. 1·5 on fluoran, crystallises from glacial acetic acid in large needles melting at 261—264°. The solution in concentrated sulphuric acid is yellow, and does not exhibit fluorescence; aqueous soda is without action, but hot alcoholic potash dissolves it, forming a reddish-yellow liquid.

2 : 7-*Diamidofluoran*, $\begin{matrix}CO\cdot O\\ | \\ C_6H_4\end{matrix}>C<\begin{matrix}C_6H_3(NH_2)\\C_6H_3(NH_2)\end{matrix}>O$, prepared by reducing the nitro-compound with stannous chloride and hydrochloric acid, crystallises from hot alcohol in small, lustrous prisms or plates, which display bright colours in polarised light. It melts at 280—282°. The solution in hot, glacial acetic acid is violet, and becomes pink on cooling. Concentrated sulphuric acid dissolves it, yielding a yellow solution, which, on heating, becomes intense cherry-red, and exhibits a yellow fluorescence when cold; the solution becomes green when diluted with water, developing a deep violet coloration with excess of caustic soda. The *hydrochloride* crystallises in aggregates of minute needles, and the *stannichloride* and *mercurichloride* are also crystalline; the *platinochloride* separates in pale, yellow needles, and the *aurichloride*, which crystallises in microscopic needles, must be precipitated from solutions containing excess of hydrochloric acid, because neutral diamidofluoran hydrochloride is immediately oxidised by gold chloride.

2 : 7-Dihydroxyfluoran (quinolphthalein), $\begin{matrix}CO.O\\ | \\ C_6H_4\end{matrix}>C<\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>O$, is produced on boiling a solution of diamidofluoran in concentrated sulphuric acid with a 2 per cent. solution of sodium nitrite; it crystallises from dilute alcohol in microscopic rhombic plates, melts at

225—227°, and is identical with the compound prepared from phthalic anhydride and quinol.

Trinitrofluoran, $C_{20}H_9N_3O_9$, obtained from fluoran by the action of nitric acid in presence of concentrated sulphuric acid, crystallises from dilute acetic acid in needles, and melts at 250°. The solution in concentrated sulphuric acid is yellow, and does not exhibit fluorescence, but becomes dark reddish-brown when heated.

Pentanitrofluoran, $C_{20}H_7N_5O_{13}$, is prepared by heating fluoran with fuming nitric and concentrated sulphuric acids on the water bath. It crystallises in rhombic leaflets on adding alcohol to its solution in hot nitrobenzene, and separates in stellar aggregates of needles on diluting the solution in glacial acetic acid with water. The compound does not melt below 335°. When gently heated with concentrated sulphuric acid, it dissolves, the colourless solution becoming reddish-brown with rise of temperature. Alcoholic potash gives rise to a reddish-yellow solution resembling the liquid obtained from trinitrofluoran.

M. O. F.

Preparation of βγ-Diphenylquinoxaline. By TH. WOLFF (*J. pr. Chem.*, 1898, **57**, 546—547).—βγ-Diphenylquinoxaline may be prepared by heating the hydrochloride of orthophenylenediamine with benzil; when cold, the melt is crystallised from alcohol, a 73 per cent. yield of the substance being obtained as white needles melting at 125—126°. The difference in the melting point of this compound as obtained by Hinsberg and König, 124° (Abstr., 1894, i, 624), and O. Fischer, 126° (Abstr., 1891, 747), is assigned by the author to the difference in the thermometer used. A. W. C.

Azophenine. By JOHN THEODORE HEWITT and HENRY E. STEVENSON (*Ber.*, 1898, **31**, 1789—1791).—The authors support the symmetrical formula employed by O. Fischer and Hepp to represent the constitution of azophenine. M. O. F.

Syntheses in the Carbazole Group. By FRITZ ULLMANN (*Ber.*, 1898, **31**, 1697—1698).—Graebe and Ullmann have shown that phenylazimidobenzene, on distillation, is converted into carbazole, nitrogen being eliminated. The following derivatives of carbazole have since been prepared by this method.

3 : 2′-Dimethylcarbazole, melting at 224°, from paratolylazimidoparatoluene; 2-chlorocarbazole, melting at 244°, from phenylazimidoparachlorobenzene; 3-amidocarbazole, melting at 235—240°, identical with the compound described by Mazzara and Leonardi; 3-methylcarbazole, melting at 207°, from paratolylazimidobenzoic acid; 1 : 2-naphthacarbazole, melting at 134·5°, described by Schöpff, and carbazole from phenylazimidobenzoic acid. 1 : 2-Naphtha-2″-methylcarbazole, melting at 181°, is obtained from *paratolylazimidonaphthalene*, which melts at 145°.

M. O. F.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Naphthalene and Naphthylic Ethers in the Presence of Aluminium Chloride. By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], **17**, 300—312).—The derivatives prepared from naphthalene have already been noticed (Abstr., 1896, i, 652).

Ethylic chloroglyoxylate reacts with α-methoxynaphthalene in the presence of aluminium chloride to form *ethylic α-methoxynaphthylglyoxylate*, $C_{10}H_6(OMe)\cdot CO\cdot COOEt$, a white, crystalline solid, melting at 70°, and boiling at 239—242° under a pressure of 10 mm. It forms a yellow, crystalline *picrate* melting at 82°, and, on hydrolysis, yields *α-methoxynaphthylglyoxylic acid*, which crystallises in small, yellowish grains melting at 164—165°. The *methylic* salt of this acid melts at 87°. When α-methoxynaphthylglyoxylic acid is treated with aniline, it yields a *phenylimide* which, on heating with dilute sulphuric acid, is converted into *α-methoxynaphthaldehyde*, a white solid melting at 34° and boiling at 200—201° under 11 mm. pressure. This forms a *hydrazone* crystallising from benzene in yellow needles melting at 185°, and is oxidised by potassium permanganate in alkaline solution to 1 : 4-methoxynaphthoic acid, previously obtained by Gattermann (*Annalen*, **264**, 61). It follows from these results that ethylic α-methoxynaphthylglyoxylate has the constitution [OMe : CO·COOEt = 1 : 4].

Ethylic β-methoxynaphthylglyoxylate, from ethylic chloroglyoxylate and β-methoxynaphthalene, forms colourless needles melting at 75° to a viscous liquid which boils at 235—238° under a pressure of 10 mm. The *picrate* crystallises in yellow needles melting at 146°. On hydrolysis, the ether yields *β-methoxynaphthylglyoxylic acid*, a yellow, crystalline solid melting at 151°, and this, on boiling with aniline, yields a *phenylimide*, boiling at 262—265° under 10 mm. pressure, which is decomposed by dilute sulphuric acid, with formation of *β-methoxynaphthaldehyde*. The latter crystallises from ether in hexagonal plates and from alcohol in long needles, both forms melting at 84° to a liquid which boils at 200—201° under 11 mm. pressure. The *hydrazone*, $C_{10}H_6(OMe)\cdot CH{:}N\cdot N{:}CH\cdot C_{10}H_6\cdot OMe$, forms brilliant needles melting at 265°, and *β-methoxynaphthoic acid*, obtained by oxidising the aldehyde with potassium permanganate in alkaline solution, melts at 176°. The constitution of β-methoxynaphthaldehyde is determined from the fact that it is identical with the product of the action of methylic iodide on the hydroxynaphthaldehyde, [COH : OH = 1 : 2], obtained by Kaufmann from β-naphthol by the action of chloroform and caustic soda. Hence it follows that ethylic β-methoxynaphthylglyoxylate has the constitution

$C_{10}H_6(OMe)\cdot CO\cdot COOEt$ [CO·COOEt : OMe = 1 : 2]. N. L.

Alkyl Derivatives of β-Naphthol. By F. Bodroux (*Compt. rend.*, 1898, **126**, 840—842).—When β-naphthol is heated with an alkylic iodide in presence of alcoholic potash, it yields compounds analogous to β-ethoxynaphthalene, $C_{10}H_7\cdot OEt$, which is already known, and which forms nacreous lamellæ melting at 36° to 36·5°. *β-Propoxynaphthalene* and *β-isopropoxynaphthalene* crystallise in long, colourless needles with a penetrating and unpleasant odour; the former melts at 39·5° to 40°, and the latter at 41°. *β-Isobutoxynaphthalene* forms nacreous lamellæ which melt at 33°. *β-Isoamoxynaphthalene* crystallises from a strongly cooled alcoholic solution in white lamellæ which melt at 26·5° and boil at 315° to 316°, the distillate readily remaining in superfusion.

All these compounds combine with picric acid in alcoholic solution, and the products crystallise in long yellow or orange needles; the

propyl compound melts at 75°, the isopropyl compound at 92°, the isobutyl compound at 80° to 80·5°, and the isoamyl compound at 90·5° to 91°. C. H. B.

Dimethyl-β-Naphthol. By EDGAR WEDEKIND (*Ber.*, 1898, **31**, 1675—1680. Compare Andreocci, Abstr., 1894, i, 205).—1 : 4-Dimethyl-2-naphthol is obtained from santonin by converting it into desmotroposantonin, reducing this with zinc dust and acetic acid, and fusing the product with caustic potash. As compared with β-naphthol, the substance is chemically inactive, for instance, it is incapable of yielding azo-compounds with diazonium salts; it is also indifferent towards nitrosodimethylaniline and nitrous acid. Moreover, attempts to convert it into the amine under conditions favourable to the production of β-naphthylamine from β-naphthol were fruitless. The *benzoyl* derivative crystallises from alcohol in long, colourless needles melting at 124—125°. The *sodium* derivative is a greyish, crystalline substance, which dissolves readily in alcohol and water. The *trinitrophenyl* ether, prepared by the action of picric chloride on the sodium derivative, crystallises from alcohol in slender, yellow needles, and melts at 189—190°. M. O. F.

Ketones Derived from Naphthalene. By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], **17**, 313).—The compounds described in a previous communication (Abstr., 1897, i, 75) have been prepared in a state of greater purity, with the result that some physical constants are slightly modified.

β-Naphthyl methyl ketone crystallises from methylic alcohol in fine, white grains melting at 53°, whilst β-naphthyl ethyl ketone, prepared in a similar manner, melts at 60°. β-Naphthyl propyl ketone crystallises from light petroleum in flat prisms melting at 52°; and its *hydrazone*, $C_{10}H_7\cdot CPr{:}N\cdot N{:}CPr\cdot C_{10}H_7$, in golden-yellow needles melting at 130°. β-Naphthyl isobutyl ketone is obtained by crystallisation from light petroleum in transparent plates melting at 36°. N. L.

Action of α-Naphthylamine on Bromotolueneazosalicylic Acid. By JOHN THEODORE HEWITT and HENRY E. STEVENSON (*Ber.*, 1898, **31**, 1785—1789).—The authors have shown that the action of aniline on orthochlorobenzeneazosalicylic acid gives rise to a compound resembling an anilide of aposafranonecarboxylic acid (Trans., 1896, **69**, 1257). When bromotolueneazosalicylic acid is heated with α-naphthylamine and the hydrochloride at 150—160°, the *compound* $C_{34}H_{24}N_3O_2Cl$ is produced; its constitution is probably represented by the formula $C_6H_3Me\langle{}^{N}_{NCl(C_{10}H_7)}\rangle C_6H_2(COOH)\cdot NH\cdot C_{10}H_7$. The base of which this substance is the hydrochloride has not been isolated. The *hydrobromide*, *iodide*, *nitrate*, and *sulphate* have been prepared. M. O. F.

Preparation and Properties of Dialkylamidoanthraquinones. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1898, **126**, 1544—1546. Compare this vol., i, 483).—3-*Dimethylamidoanthraquinone*, obtained when dimethylamidobenzoylbenzoic acid (1 part) is heated with concentrated sulphuric acid (10 parts) at 175—180°, crystallises

from benzene or toluene in red needles melting at 181°; the yield is 35—40 per cent. of the theoretical, oxidation products being formed at the same time.

Dimethylamidoanthranol, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{\cdot CO\cdot}>C_6H_3\cdot NMe_2$, is obtained when dimethylamidobenzylbenzoic acid is heated with 12 times its weight of concentrated sulphuric acid at 80°; the product is poured into water and the yellow solution neutralised with sodium carbonate. The precipitate thus obtained crystallises from benzene in yellow needles. It is extremely unstable, like all anthranols, and is readily oxidised to dimethylamidoanthraquinone; the oxidising agent recommended is ferric chloride.

Diethylamidoanthraquinone, obtained from diethylamidobenzoylbenzoic acid, crystallised in red plates melting at 162°. J. J. S.

Derivatives of Fluorenone. By Fritz Ullmann and Ed. Mallett (*Ber.*, 1898, **31**, 1694—1696).—3-*Methylfluorenone*, $\genfrac{}{}{0pt}{}{C_6H_3Me}{C_6H_4}>CO$, is obtained by the action of nitrous acid on orthamidophenyl paratolyl ketone, the synthesis being analogous to the production of fluorenone from orthamidobenzophenone; it crystallises from dilute alcohol in yellow leaflets, and melts at 66·5° (corr.). A small proportion of orthohydroxyphenyl paratolyl ketone is produced along with it.

Nitrochlorobenzophenone [$COPh : Cl : NO_2 = 1 : 2 : 5$], prepared by heating the chloride of 2 : 5-chloronitrobenzoic acid with benzene and aluminium chloride on the water bath, crystallises from alcohol in white needles, and melts at 86° (corr.).

Nitramidobenzophenone [$COPh : NH_2 : NO_2 = 1 : 2 : 5$], which is formed by the action of alcoholic ammonia on the foregoing substance, crystallises in yellowish-red prisms with blue reflex; it melts at 161·5° (corr.). 2-Nitrofluorenone, $\genfrac{}{}{0pt}{}{NO_2\cdot C_6H_3}{C_6H_4}>CO$, is prepared by the action of nitrous acid on nitramidobenzophenone, and is identical with the product obtained by Schultz on treating fluorenone with nitric acid.

Nitrohydroxybenzophenone [$COPh : OH : NO_2 = 1 : 2 : 5$], a bye-product of the action of nitrous acid on nitramidobenzophenone, separates from alcohol in lustrous, white crystals, and melts at 124—124·5°.

M. O. F.

Action of the Silent Electric Discharge on Liquid Dielectrics. By Marcellin P. E. Berthelot (*Compt. rend.*, 1898, **126**, 691—694).—Dry terebenthene, when subjected to the action of the silent electric discharge, yields a small quantity of diterebenthene, but otherwise remains unaltered. Olive oil yields a small quantity of a blackish product insoluble in ether, oil, and all the usual solvents. Except for the difference in colour, it resembles the polymeride formed in presence of nitrogen (this vol., i, 559). Alcohol, when the action is prolonged, yields hydrogen and ethane, and the liquid contains some aldehyde and a hydrocarbon which seemingly contains less hydrogen than the olefines, and has a feeble reducing action on ammoniacal silver nitrate. C. H. B.

Spanish Essence of Lavender. By EUGÈNE CHARABOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 378—380).—Two specimens of Spanish essence of lavender, manufactured in 1895 and 1896 respectively, were found to differ considerably in composition from the French essence. The density was higher, and the rotatory power positive instead of negative, whilst the linalol and linalol acetate, which are the essential constituents of the French essence, were replaced by borneol and a small percentage of ethereal salts. The following analytical results were obtained.

	1895.	1896.
Sp. gr. at 15°	0·916	0·912
Rotatory power	16° 25′	13° 20′
Ethereal salts, as $C_{10}H_{17}OAc$	3·15 per cent.	3·4 per cent.
Alcohols, as $C_{10}H_{17}OH$	44·5 ,,	50·5 ,,

French essence of lavender has a sp. gr. at 15° = 0·885—0·895 and a rotatory power = − 5° to − 8°. N. L.

Essence of Cedar-wood. By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], 17, 485—489).—Essence of cedar-wood consists almost entirely of a liquid sesquiterpene (*cedrene*), and a solid substance (*cedrol*), having the characters of a tertiary alcohol.

Cedrene, $C_{15}H_{24}$, is a slightly viscous, colourless liquid, boiling at 131—132° under a pressure of 10 mm. It is lævorotatory: $\alpha_D = -17° 54'$. Cedrene absorbs bromine and halogen acids, but the compounds produced are very unstable. When oxidised by chromic acid in acetic acid solution, it yields *cedrone*, $C_{15}H_{24}O$, a liquid of ketonic character, boiling at 147—151° under a pressure of 7·5 mm.; it does not combine with sodium hydrogen sulphite, but yields iodoform with sodium hypobromite and potassium iodide so that it contains the acetyl group. It also forms an *oxime*, which boils at 175—180° under 8 mm. pressure, and is converted by acetic anhydride into an *acetate* boiling at 185—190° under a pressure of 9 mm. When reduced with sodium in ethereal solution, cedrone is converted into the alcohol *isocedrol*, $C_{15}H_{26}O$, which boils at 148—151° under 7 mm. pressure, and forms a *benzoate* boiling at 221—223° under 6 mm. pressure. Cedrene is oxidised by excess of chromic acid in sulphuric acid solution to a viscous *acid*, $C_{12}H_{18}O_3$, boiling at 220—230° under a pressure of 9 mm.

Cedrol, $C_{15}H_{26}O$, crystallises from methylic alcohol in colourless needles melting at 84°, and is optically active. On heating with acetic anhydride at 100°, it yields an *acetate*, $C_{17}H_{28}O_2$, boiling at 157—160° under 8 mm. pressure, and is at the same time partially dehydrated with production of a sesquiterpene; the same dehydrating action is brought about by benzoic chloride and by chromic acid. N. L.

Santal Essence and its Adulteration. By W. DULIÈRE (*J. Pharm.*, 1898, [vi], 7, 332—336; from *Bull. Acad. roy. Belg.*, 1897).—The following data are given for the essence. Sp. gr. at 15 = 0·973—0·976. Solubility in alcohol at 70°, 1 part in 5 if the essence is fresh or well preserved, otherwise 1 in 15. Saponification number, maximum = 12·6. Percentage of santalol = 94. Concentrated sulphuric acid should cause solidification to a dry and friable mass. Iodine number after 3 hours = 157·6—159·25. It should give practically no coloration with

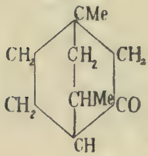
Dragendorff's reagent (bromine and chloroform), with a solution of zinc chloride in hydrochloric acid, or with Conrady's reagent. J. J. S.

Essence of Geranium. By EUGÈNE CHARABOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 489—492).—The rotatory power of a number of specimens of essence of geranium was found to be lowered by saponification, a fact which indicates the presence of lævorotatory ethereal salts. These appear to be absent from essence of palmarosa. N. L.

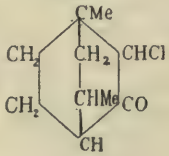
Semicarbazones of α-Ionone. By J. C. W. FERDINAND TIEMANN *Ber.*, 1898, 31, 1736—1739. Compare this vol., i, 376).—As already stated, purified α-ionone yields a semicarbazone which, after crystallisation from boiling petroleum, melts at 107—108°. If this compound is recrystallised several times from 60 per cent. alcohol, or repeatedly precipitated by water from its solution in strong alcohol, the *semicarbazone* which melts at 137—138° is obtained; the ketone regenerated from this by the action of alcoholic sulphuric acid is identical with α-ionone in all respects. M. O. F.

Constitution of Camphor and Derived Nitrophenols. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1897, [iii], 17, 202—204).—In order to explain the formation of nitrophenols, and more especially of dinitro-orthocresol, the author suggests a slight modification in Bouveault's formula for camphor. The following constitutional formulæ are suggested.

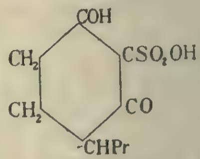
Camphor.



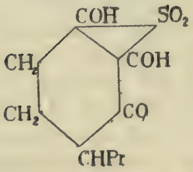
Monochlorocamphor.



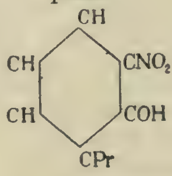
Camphosulphonic acid.



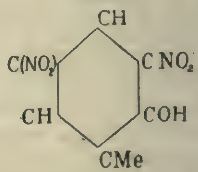
Camphosulphone.



Propylnitrophenol.



Dinitro-orthocresol.



N. L.

Action of Nitrous Acid on Camphoroxime. By ANGELO ANGELI (*Gazzetta*, 1898, 28, i, 11—18).—In face of the criticisms of Mahla and Tiemann (Abstr., 1897, i, 85), the author adheres to his previous view of the constitutions of pernitrosocamphor and of isocamphor (Angeli and Rimini, Abstr., 1897, i, 88). It is unlikely that pernitrosocamphor is a camphenylnitramine, because it does not react with diazomethane, although Pechmann has shown (Abstr., 1897, i, 264) that nitramines react violently with this substance. W. J. P.

Nitrogen Derivatives of Santonic Acid. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 1680—1682).—Unlike santoninic acid, santonic acid dissolved in alkali displays great activity towards diazonium chlorides.

The *compound*, $C_{27}H_{28}N_4O_4$, obtained by the action of diazotised aniline on santonic acid dissolved in caustic soda, is precipitated on adding hydrochloric acid to the solution; it crystallises from alcohol, and melts at 125—130°. The empirical formula shows that two benzeneazo-residues become attached to the santonic complex.

Reduction with stannous chloride and hydrochloric acid changes the intensely yellow colour of the compound to deep red, water precipitating a bright red substance from the liquid. M. O. F.

Action of Soluble Ferments on Gentianose. By EMILE BOURQUELOT (*Compt. rend.*, 1898, **126**, 1045—1047).—The gentians contain a soluble ferment, analogous to invertin, which hydrolyses gentianose. Diastase and emulsin have no similar effect, but invertin from yeast, and the soluble ferments produced during the growth of *Aspergillus niger*, also hydrolyse the gentianose. The action of invertin is slower than with saccharose, and the hydrolysis is incomplete, whereas with the ferments from *Aspergillus*, which include ferments of polyglucoses, the hydrolysis is complete, and it would follow that the glucoses exist in the molecule of gentianose, partly as saccharose and partly as a polyglucose. C. H. B.

Products obtained by the Hydrolysis of Ouabain. By ALBERT ARNAUD (*Compt. rend.*, 1898, **126**, 1208—1211. Compare this vol., i, 377).—Ouabain is only completely hydrolysed by dilute sulphuric acid (2 per cent.) after some 24 hours boiling; the two products are an insoluble resin and rhamnose, the amount of the latter being always 21·10—21·80 per cent. of the ouabain employed (calculated from the hydrated ouabain, $C_{30}H_{46}O_{12} + 9H_2O$). The amount of resin varies from 47·5 to 49 per cent. This resin, which has not been obtained in a crystalline state, is readily soluble in warm alcohol, in methylic alcohol, ether, or alkalis, and after drying at 135° in an atmosphere of carbonic anhydride has the composition $C_{24}H_{28}O_4$.

The hydrolysis of ouabain is probably represented by the equation $C_{30}H_{46}O_{12} + H_2O = C_6H_{12}O_5 + C_{24}H_{36}O_8$, the resin $C_{24}H_{28}O_4$ being obtained from the compound $C_{24}H_{36}O_8$ by the loss of $4H_2O$.

J. J. S.

Action of Alkalis on Ouabain. By ALBERT ARNAUD (*Compt. rend.*, 1898, **126**, 1280—1282).—Sodium, potassium, and barium hydroxides do not hydrolyse ouabain, either in the cold or on boiling, they yield a hydrated derivative of ouabain, but no decomposition ensues; the reaction is practically the same at 140°, even with concentrated alkalis. The product, *ouabic acid*, $C_{30}H_{48}O_{13}$, is a monobasic acid capable of decomposing carbonates, reddening blue litmus, and yielding salts most of which are readily soluble in water. It is an amorphous, gummy substance which is lævorotatory, readily soluble in water or in alcohol, insoluble in ether, and melts at about 235°, but decomposes at the same time. When hydrolysed by boiling with dilute mineral acids, it yields rhamnose and a resin, probably identical with that obtained from ouabain (see previous abstract). The *sodium* salt, $C_{30}H_{47}NaO_{13} + 3H_2O$, and *potassium* salt are best obtained

by dissolving the acid in about 10 times its weight of alcohol, and then adding the requisite quantity of sodium or potassium ethoxide. The *barium*, *strontium*, and *lead* salts have also been prepared, the barium salt has a specific rotatory power $[\alpha]_D = -46.40$ at 20°. Ouabic acid can also be obtained by heating ouabain with water at 180°, but if the solutions are as concentrated as 15—20 per cent. hydrolysis also ensues. When fused with potash or soda, ouabain yields carbonic anhydride, oxalic acid, and a small quantity of resin.

J. J. S.

Pimpinellin. By G. Heut (*Arch. Pharm.*, 1898, **236**, 162—164).—Pimpinellin, the bitter principle of the root of *Pimpinella Saxifraga*, crystallises from dilute alcohol in long, colourless, lustrous needles which melt at 106°, and not at 97° as stated by Buchheim (*Arch. Pathol.*, 1872, 37). With concentrated sulphuric acid, it gives a green coloration, and readily dissolves in dilute caustic potash, yielding a solution from which it is precipitated unchanged by carbonic anhydride; with its alcoholic solution, lead acetate gives no precipitate. Buchheim's analyses (*loc. cit.*) point to its composition being $C_{21}H_{16}O_8$, but those of the author agree more closely with the formula $C_{14}H_{12}O_5$.

Besides pimpinellin, there is present in an alcoholic extract of the root of *Pimpinella Saxifraga*, a yellow, crystalline *substance* which melts at 148°, resolidifies at 138°, and is not decolorised by treatment with animal charcoal.

W. A. D.

Bark of Hamamelis virginica L. By Fritz Grüttner (*Arch. Pharm.*, 1898, **236**, 278—320).—On extracting the bark of *Hamamelis virginica L* with ether, a greenish-brown mass is obtained, which may be separated into two portions by means of light petroleum. The insoluble *wax* is still yellowish-white, even after repeated crystallisation from alcohol, and melts at 72°, whilst the soluble *fat*, which is dark green, consists principally of the ethereal salts of phytosterol, $C_{26}H_{44}O + H_2O$ (melting at 137°), and oleic and palmitic acids, together with an acid containing a higher percentage of carbon, probably stearic acid.

The bark, freed from fat, was then extracted with alcohol, and the extract treated with water, when a small quantity of insoluble phlobaphen was precipitated, and two soluble tannin substances obtained, (*a*) "*Glucosidetannin*" is a reddish-brown powder, soluble in hot water, and possessing a very astringent and bitter taste. When boiled with 2 per cent. sulphuric acid, it is converted into gallic acid and a sugar. (*b*) *Hamamelitannin*, $C_{14}H_{14}O_9 + 5H_2O$, as obtained from the bark in the ordinary manner, is an amorphous substance, but can be crystallised from dilute solutions in the form of fine, colourless needles melting at 74—75°, and after drying at 100°, at 115—117°. On further heating to 130°, the substance again becomes solid, is coloured brown at 198°, and melts and gives off gas at 220°. It is optically active $[\alpha]_D = +35.43°$, and possesses all the properties of a tannin. No crystalline salts could be obtained.

On hydrolysis, hamamelitannin is entirely converted into gallic acid, thus proving that it is not a glucoside, but contains two gallic

acid residues in the molecule. It contains no methoxyl group, and phenylhydrazine is without action on it. On acetylation, it gives a rose-coloured *acetyl* derivative, and when benzoylated by Baumann's method, a *benzoyl* derivative, $C_{14}H_9Bz_5O_9$, is produced as a yellowish-white powder melting at 125—132°.

The bark also contains gallic acid and glucose in the free state.

A. W. C.

Aloes. By Alexander Tschirch and Gullow Pedersen (*Arch. Pharm.*, 1898, **236**, 200—212).—The *resin* prepared by digesting Barbadoes aloes with strong alcohol, and precipitating the filtered extract with water, forms a brownish powder which is easily soluble in alkalis, but insoluble in most organic solvents. On hydrolysis with dilute sulphuric acid, or better, with sodium hydrogen carbonate, it yields cinnamic acid, and a greyish-brown powder, *aloresinotannol*, $C_{22}H_{26}O_6$, which dissolves readily in potash, aqueous ammonia, ethylic and amylic alcohols, is nearly insoluble in ether, chloroform, benzene, and ethylic acetate, and yields a *benzoate*, $C_{22}H_{24}O_6Bz_2$. The resin of Cape aloes yields, on hydrolysis, the same aloresinotannol together with paracoumaric acid. Eigel (Abstr., 1887, 1109) has stated that the latter is also formed on hydrolysing Barbadoes aloes with dilute sulphuric acid; the author, however, finds that, in this case, cinnamic acid alone is obtained.

On extracting with ether an aqueous solution of Barbadoes aloes from which the resin and barbaloin have previously been removed, an orange-yellow colouring matter is obtained which crystallises from alcohol in microscopic needles, readily sublimes, melts at 216°, and has the properties of an *emodin*, $C_{15}H_{10}O_5$. The latter is a powerful diarrhœtic, and enhances the peristaltic movement; it is also present in several varieties of aloes, and on its presence Bornträger's test (*Zeit. anal. Chem.*, 1880, 165) depends. The latter apparently is not characteristic of aloes; it gives positive results with several other plants, and negative ones with Natal and Socotra aloes, which do not contain emodin; it is probably characteristic of a methylhydroxyanthraquinone group.

Although purified barbaloin does not give the Bornträger reaction, it answers to this test after being subsequently crystallised from alcohol; this is probably due to the action of the air transforming a portion into emodin, since an appreciable quantity of the latter is formed when air is blown through a solution of barbaloin in 1 per cent. caustic potash.

Carefully purified anhydrous barbaloin melts at 147°, and has the composition $C_{16}H_{16}O_7$, ascribed to it by Groenewold (Abstr., 1890, 639); it crystallises with $3H_2O$, of which two are lost at 100°, and the third when dried at 100—110° in a stream of hydrogen. When fused with caustic potash, or heated with 10 per cent. sulphuric acid and steam blown through the mixture, an intensely black powder, *alonigrin*, $C_{22}H_{18}O_8$, is formed, which is readily soluble in alkalis, but insoluble in the ordinary organic solvents.

In conclusion, the author confirms Flückiger's formula, $C_{34}H_{38}O_{15} + 5H_2O$, for socaloin (this Journal, 1872, 299), obtained from *Aloë*

socotrina liquida, and gives the following analysis of a specimen of Barbadoes aloes.

Resin.	Barbaloin.	Emodin.	Ash.	Water.	Amorphous constituent, soluble in water.
12·65	12·25	0·15	1·75	10·5	62·7

W. A. D.

Oroselone and Peucedanin. By MAXIMILIAN POPPER (*Monatsh.*, 1898, **19**, 268—279).—Peucedanin, from *Peucedanum officinale*, on treatment with hydrochloric acid, yields oroselone (m. p. 177°), but that obtained from *Imperatoria Ostruthium* gives rise to a totally different substance which decomposes at 240°. Imperatorin from the latter plant, and peucedanin from *Peucedanum officinale* are considered to be identical on account of their similar physical properties and composition, and because they were formerly both supposed to give oroselone and angelic acid on treatment with caustic alkalis; but Hlasiwetz and Weidel found that peucedanin, under these conditions, gave no angelic acid, and hence the identity of these two substances is open to question.

The author has prepared peucedanin from the root of *Peucedanum officinale*, and finds that the product, after crystallisation from alcohol and light petroleum, is not homogeneous, but can be separated into two constituents differing in their solubility in dry ether.

The less soluble part, after many fractional crystallisations, yields a substance having the appearance of peucedanin, but differing from it in composition and melting point. This compound, $C_{14}H_{11}O_3{\cdot}OMe$, which the author proposes to call *oroselonemonomethylic ether*, melts at 105° (peucedanin prepared by Hlasiwetz and Weidel melts at 81—82°), distils without decomposition at 276—281° under 17 mm. pressure, crystallises from ether in yellowish-white needles, and dissolves in alkalis, forming a yellow solution; on treatment with hydrochloric or hydriodic acid, one methyl group is eliminated, and oroselone, $C_{14}H_{12}O_4$, is produced. The latter is identical with Hlasiwetz and Weidel's preparation, but its acetyl derivative, $C_{14}H_{11}O_3{\cdot}OAc$, as prepared by the author, melts at 118°, whilst that obtained by the other investigators melts at 123°.

The more soluble part, after fractional crystallisation from benzene and ether, yields well-defined, yellowish-white prisms melting at 85—93°; the results of analysis point to its being an oroselone dimethylic ether, but a determination of methoxyl indicates that the substance, in spite of its definite crystalline form, probably consists of a mixture of mono- and di-methylic ethers of oroselone.

G. T. M.

Chloroproteinochrome. By C. BEITLER (*Ber.*, 1898, **31**, 1604—1610. Compare Nencki, Abstr., 1895, ii, 233).—It has been shown by Gmelin that a red colouring matter is formed on adding chlorine water to the products of the pancreatic digestion of egg-albumin; this the author calls *chloroproteinochrome*, and summarises the results of his investigation in the following terms. 1. The albumin molecule contains a complex, chromogenic group which is set free by

pancreatic digestion, and is precipitated by chlorine water in the form of a red chloro-compound. 2. Chloroproteinochrome, the product of this action, appears to have the composition expressed by the formula $C_{96}H_{116}Cl_3N_{21}O_{31}S$; it is decomposed by cold solutions of alkalis and metallic salts, and also by boiling alcohol and ethylic acetate, yielding indefinite substances. 3. The proteinochromogen, being represented by the approximate formula $C_{96}H_{119}N_{21}O_{31}S$, contains a larger proportion of carbon, and smaller proportions of nitrogen and hydrogen, than proteid substances ; it is likewise very unstable, but diffuses through membranes, and is precipitated from aqueous solution by phosphotungstic acid, but not by metallic salts. The proteinochromogen cannot, however, be obtained by decomposing the substance which it yields with phosphotungstic acid. M. O. F.

Antimony Pentafluoride and some of its Double Salts with Organic Bases. By PAUL REDENZ (*Arch. Pharm.*, 1898, **236**, 263—277).—When antimonic acid is dissolved in pure hydrofluoric acid, and the solution evaporated, a very hygroscopic, syrupy mass is left which is not completely soluble in water ; neither by this method nor by dissolving antimonic oxide in hydrofluoric acid could a crystalline antimony pentafluoride be obtained. For the preparation of the following substances, a solution of antimony pentafluoride was obtained from the firm of de Haen in Hanover.

Antimony pentafluoride pyridine hydrochloride, SbF_5,C_5NH_5,HCl, obtained by evaporating a solution of antimony fluoride in pyridine hydrochloride, forms glistening needles melting at 176—177° ; it is decomposed by water and alcohol. A second *compound*, probably of the formula $2SbF_5,5(C_5NH_5,HCl)$, crystallising in rhombohedra, and melting at 180°, was also obtained. The estimation of antimony was done electrolytically, by warming the double salt with caustic soda, to get rid of pyridine, adding sodium sulphide solution, and electrolysing : and the fluorine was determined by Oettel's method (*Zeit. anal. Chem.*, **25**, 505).

Antimony pentafluoride picoline hydrochloride, prepared in a similar manner, crystallises in glistening needles melting at 117° ; the *collidine hydrochloride* compound is a yellow, crystalline precipitate, whilst the *quinoline hydrochloride* compound crystallises in glistening, silky needles melting at 200°.

With paratoluidine hydrochloride, two *compounds* are obtained, the one, $2SbF_5,5(C_6H_4Me\cdot NH_2,HCl)$, crystallising in needles and decomposing at 100—110°, and the other, $3SbF_5,7(C_6H_4Me\cdot NH_2,HCl)$, in leaflets melting at 232°.

Nicotine and coniine hydrochlorides give no crystalline compounds with antimony pentafluoride.

The *compound* with quinine hydrochloride forms lemon-yellow crystals soluble in hot water without decomposition and melting at 213—214°. A. W. C.

Morpholine Bases. By LUDWIG KNORR (*Annalen*, 1898, **301**, 1—10. Compare Abstr., 1889, 1218, and 1897, i, 314).—Morpholine, C_4NOH_9, which is a colourless, limpid, alkaline liquid having the

odour of ammonia and piperidine, is excessively hygroscopic, and is very volatile in atmospheres of ether and water vapours. It is miscible in all proportions with common solvents, and develops heat when dissolved in water; the solution affects the skin like caustic potash, and at high temperatures will attack glass. The base boils at 128—130°, and has a sp. gr. = 1·0007 at 20°/4°; the refractive index $[n]_D = 1·4540$, whence the molecular refraction 23·54. Morpholine absorbs moisture and carbonic anhydride from the air, and fumes in moist air; carbonic anhydride precipitates the *carbamate*, $OH·CO(C_4H_8ON)_2$, in white crystals from the ethereal solution of the base.

The *hydrochloride* is readily soluble in water, and melts and decomposes at 174—177°; the *aurochloride* and *platinochloride* melt and decompose at 240° and 210° respectively. The *picrate* and *picrolonate* dissolve with difficulty in water, and melt at 145—147° and 255° respectively. Aqueous morpholine yields precipitates with many of the agents used for recognising alkaloids.

Nitrosomorpholine, which melts at 29°, and boils at 224—224·5° under a pressure of 747 mm., has the odour of nitrosopiperidine, and gives Liebermann's reaction. *Benzoylmorpholine* crystallises from ether in prisms, and melts at 74—75°. Morpholine *urethane* boils at 220—221° under a pressure of 746 mm.; the *carbamide* derivative melts at 110—113°.

Hydroxyethylmorpholine, $OH·CH_2·CH_2·N{<}{\substack{CH_2·CH_2\\CH_2·CH_2}}{>}O$, is prepared by the action of ethylenic oxide on morpholine, and also by heating triethanolamine (trihydroxytriethylamine) with 70 per cent. sulphuric acid at 160—170°; it boils at 227°.

Morpholine is indifferent towards water at 200°, 10 per cent. caustic soda and concentrated hydrochloric acid at 160°, and phenylhydrazine at 200°; it undergoes slow oxidation with acid solutions of potassium permanganate, changing more rapidly in presence of acids.

M. O. F.

1-Methylmorpholine. By LUDWIG KNORR and HERMANN MATTHES (*Annalen*, 1898, **301**, 10—14).—1-Methylmorpholine, prepared by heating diethanolmethylamine (this vol., i, 399) with 70 per cent. sulphuric acid at 160° during 16 hours, is a colourless, limpid, volatile liquid, having a powerful ammoniacal odour. The base boils at 115—116° under a pressure of 750 mm., and has a sp. gr. = 0·9051 at 20°; the refractive index $[n]_D = 1·4332$, whence the molecular refraction 29·01. Methylmorpholine is indifferent towards methylamine solution at 180°, and 30 per cent. hydrochloric acid at 250°; hydriodic acid and ammonium iodide at 240° regenerate morpholine. The ordinary alkaloid reagents yield characteristic precipitates with the base.

The *picrate*, which is almost insoluble in alcohol and ether, melts at 225—226°. The *ethiodide* is excessively hygroscopic, and melts at 165—166°.

M. O. F.

1-Ethylmorpholine. By LUDWIG KNORR and WERNER SCHMIDT (*Annalen*, 1898, **301**, 14—18).—1-*Ethylmorpholine*, prepared by heating diethanolethylamine (this vol., i, 399) with 70 per cent. sulphuric

acid at 160° during 18 hours, is a colourless, limpid oil having a powerful ammoniacal odour; it boils at 138—139° under a pressure of 751 mm., and has a sp. gr. = 0·8996 at 20°/4°; the refractive index $[n]_D = 1·4400$, whence the molecular refraction 33·758. Alkaloid reagents give characteristic precipitates. The *hydrochloride* is colourless and hygroscopic; the *picrate* and *platinochloride* melt at 189—190° and 197—198° respectively. The *aurochloride* crystallises in golden prisms containing $1H_2O$ and melting at 86—89°; in the anhydrous condition it melts at 125°. The *methiodide* is identical with the ethiodide of methylmorpholine described in the foregoing abstract; the *methoxide* is an oil which yields aldehyde spontaneously.

A tabular comparison of the three morpholine bases is appended to the paper. M. O. F.

Dimethylpiperazine and its Phenolic Derivatives. By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1898, **126**, 1573—1575).—It has been previously shown that piperazine reacts with phenolic carbonates yielding aromatic diurethanes of the type

$$RO{\cdot}CO{\cdot}N{<}{\genfrac{}{}{0pt}{}{CH_2{\cdot}CH_2}{CH_2{\cdot}CH_2}}{>}N{\cdot}COOR.$$

Dimethylpiperazine, however, behaves in quite a different manner, carbonic anhydride being evolved and a diphenolic derivative of the type $OH{\cdot}R{\cdot}NH{<}{\genfrac{}{}{0pt}{}{CHMe{\cdot}CH_2}{CH_2{\cdot}CHMe}}{>}NH{\cdot}R{\cdot}OH$ formed.

Dimethylpiperazine diphenate, obtained by heating the base and phenyl carbonate in molecular proportion with alcohol (93 per cent.) for three-quarters of an hour, crystallises in hard crystals when the solution is concentrated to about one-third. It dissolves in water, alcohol, ether, benzene, nitrobenzene, or glycerol, melts at 86°, and yields phenol when treated with acids.

Dimethylpiperazine diguaiacolate crystallises in fine, light needles melting at 66—67°.

Dimethylpiperazine di-α-naphthate is soluble in warm water, also in alcohol, chloroform, or nitrobenzene, but only sparingly in ether or benzene, and melts at 147°. The *β-naphthate*, which is much more soluble in alcohol than the α-compound, melts at 93°.

The authors question the constitution usually assigned to dimethylpiperazine. J. J. S.

Tropinepinacone. By RICHARD WILLSTÄTTER (*Ber.*, 1898, **31**, 1672—1675).—In preparing large quantities of ψ-tropine by reducing tropinone with sodium or sodium amalgam, this substance is obtained as a bye-product.

Tropinepinacone, $C_{16}H_{28}N_2O_2$, which is insoluble in cold water, and dissolves with extreme difficulty even in boiling water, crystallises from alcohol in lustrous, four-sided plates and elongated prisms; it melts at 188°, distils without decomposing, and can be sublimed. The *hydrochloride* dissolves very readily in water, and the *mercurichloride*, which is almost insoluble in cold water, crystallises from the hot solution in thin, lustrous needles. The *platinochloride*, when crystallised slowly, separates in four-sided plates containing $2H_2O$; it melts and

decomposes at 275°. The *aurichloride* melts and effervesces at 228—229°, and the *picrate* decomposes above 300°. M. O. F.

Benzylidenetropinic Acid. By RICHARD WILLSTÄTTER (*Ber.*, 1898, **31**, 1587—1592. Compare this vol., i, 159).—Oxidation with chromic and sulphuric acids converts dibenzylidenetropinone into benzylidenetropinic acid, which is dibasic and unsaturated; the production of this compound is regarded by the author as confirming the view that tropinic acid contains an acetic acid residue (*loc. cit.*); its unsaturated character indicates the presence of the group C:CHPh in dibenzylidenetropinone, the latter substance and benzylidenetropinic acid being represented therefore by the formulæ

$$\begin{array}{l} CH_2-CH-C{:}CHPh \\ \vert \qquad\quad NMe \quad CO \\ CH_2-CH-C{:}CHPh \end{array} \quad \text{, and} \quad \begin{array}{l} CH(COOH)\cdot NMe \\ CH_2 \text{———} CH_2 \end{array}\!\!>CH\cdot C(COOH){:}CHPh$$

respectively.

Dibenzylidenetropinone is prepared from tropinone and benzaldehyde more conveniently by the agency of alcoholic soda than with hydrochloric acid. Owing to the highly stable and sparingly soluble character of dibenzylidenetropinone *chromate*, which separates in microscopic, yellow prisms during oxidation, this operation must be conducted under specific conditions.

Benzylidenetropinic acid, $C_{15}H_{17}NO_4$, dissolves in 12 parts of cold, 3 parts of hot water, and crystallises in colourless, lustrous prisms containing $1H_2O$; it melts and begins to decompose at 190—191°, and is extremely hygroscopic in the anhydrous state. It dissolves with difficulty in hot acetone and alcohol, is scarcely soluble in chloroform, and insoluble in ether; the aqueous solution readily dissolves silver oxide, yielding a metallic mirror when gently heated. Both acid and alkaline solutions of benzylidenetropinic acid immediately decolorise potassium permanganate, when the odour of benzaldehyde becomes perceptible; lead peroxide liberates carbonic anhydride from the aqueous solution. The *hydrochloride* dissolves with difficulty in cold alcohol, but is freely soluble in water; it crystallises in prisms, and melts and decomposes at 244°; the *hydrobromide*, which crystallises from water in lustrous prisms and small, four-sided plates, melts and decomposes at 252—253°. Gold chloride yields the *aurichloride*, $(C_{15}H_{17}NO_4)_2,HAuCl_4$, which crystallises in yellow, anhydrous leaflets, and decomposes at 192—193°; when this substance is recrystallised several times, the *aurichloride*, $C_{15}H_{17}NO_4,HAuCl_4$, is obtained as an oil which slowly crystallises in prisms. The *methylic* salt dissolves readily in alcohol, wood spirit, and acetone, separating in thin leaflets and flattened needles on addition of water; it melts at 67—69°.

M. O. F.

Alkaloids of Corydalis. By ERNST SCHMIDT (*Arch. Pharm.*, 1898, **236**, 212—214).—Experiments carried out, at the author's suggestion, by W. H. Martindale, show that dehydrocorydaline (compare Ziegenbein, Abstr., 1897, i, 175, and Dobbie and Marsden, Trans., 1897, 657) can be conveniently prepared by adding bromine dissolved in

alcohol to an alcoholic solution of corydaline, and crystallising the resulting *perbromide*, $C_{22}H_{23}NO_4,HBr,Br_2$, from boiling alcohol. The formation of an optically inactive corydaline by the reduction of dehydrocorydaline (Dobbie and Marsden, *loc. cit.*) is confirmed by the author; *i*-corydaline differs from natural corydaline in the greater ease with which its salts crystallise, and in yielding an *aurichloride*, $C_{22}H_{27}NO_4,HAuCl_4 + 4H_2O$, of normal composition, that obtained from natural corydaline having the abnormal constitution $(C_{22}H_{27}NO_4,HCl)_2,AuCl_3$. Attempts to resolve *i*-corydaline into its optically active components, by means of its thiocyanate (compare Davis, Abstr., 1897, i, 174), failed.

From Ziegenbein's results (*loc. cit.*), the author concludes that, of the alkaloids of *Corydalis cava*, only corydaline and corybulbine are closely related; and that the views of Freund and Josephi (Abstr., 1894, i, 100) as to the relationship of corydaline and bulbocapnine are incorrect. In support of this opinion, Herzig and Meyer's statement (this vol., i, 53) that bulbocapnine contains one $N \cdot CH_3$ group, whilst in corydaline this group is absent, is quoted. W. A. D.

Corydaline. By W. H. Martindale (*Arch. Pharm.*, 1898, **236**, 214—246).—The corydaline used was prepared from the bulbs of "*Corydalis cava*" according to methods previously described, 10 kilograms of the bulbs yielding 90 grams of the alkaloid in colourless, prismatic crystals melting at 134—135°.

The following salts were prepared in order to compare their properties with those of inactive corydaline, and also on account of the different properties ascribed to them by various investigators.

The hydrochloride obtained by passing hydrogen chloride into an ethereal solution of the base is a viscid, green mass, crystallising with difficulty from alcohol, and then containing $1C_2H_6O$, or from water when it contains $2H_2O$.

The hydrobromide, hydriodide, nitrate, and aurichloride, have the properties ascribed to them by Ziegenbein (Abstr., 1897, i, 175); the acid sulphate, $C_{22}H_{27}NO_4,H_2SO_4 + 4H_2O$, obtained by dissolving the base in dilute sulphuric acid, forms groups of transparent plates; the platinochloride melts at 227°; and the thiocyanate, produced by adding thiocyanic acid to an alcoholic solution of the base, crystallises in plates melting at 208° and becoming green on exposure to the air.

Dehydrocorydaline hydriodide, $C_{22}H_{23}NO_4,HI + 2H_2O$, prepared according to Ziegenbein's directions (*loc. cit.*), forms lemon-yellow, transparent, prismatic plates easily soluble in hot water.

i-*Corydaline*, obtained by reducing the last-named compound with zinc and sulphuric acid, separates from alcohol in transparent, prismatic crystals melting at 135°. It is inactive, tasteless, and more stable on exposure to air than corydaline itself.

The *hydrochloride*, $C_{22}H_{27}NO_4,HCl + 2H_2O$, forms efflorescent, highly refractive, prismatic crystals; the dried salt melts at 230—240°; the *hydrobromide* is crystalline, melting and decomposing at 200°; the *nitrate* separates from alcohol in clusters of small, yellow needles; the *sulphate*, $C_{22}H_{27}NO_4,H_2SO_4,2H_2O$, forms transparent plates, the *aurichloride*, $C_{22}H_{27}NO_4,HAuCl_4 + 4H_2O$, easily soluble, yellow needles, and

the *platinochloride*, microscopic crystals melting at 230°. The *thiocyanate*, obtained by the action of thiocyanic acid on an alcoholic solution of the base, forms transparent crystals melting at 205° and becoming green on exposure to air or light. It could not be separated into left- and right-handed modifications, as in the case of *i*-lupanine (compare Davis, Abstr., 1897, i, 174).

i-*Corydaline methiodide* crystallises in plates melting at 185°, and is converted by the action of excess of silver chloride into the *methochloride*, crystallising in yellow needles. Its *aurichloride* forms glistening, dark-red crystals melting at 170—172°, and its *platinochloride* pale yellow needles melting at 222°.

When the methochloride is acted on with sodium hydroxide, it is converted into *methyl*-i-*corydaline*, $C_{22}H_{26}MeNO_4$, forming flakes or brown, oily drops, which solidify when cooled; from alcohol, it may be obtained in transparent crystals melting at 224°. The *hydrochloride* crystallises with $3H_2O$ in transparent prisms, and yields an *aurochloride* melting at 205°, and a *platinochloride* melting at 220°.

A table is given containing the melting points and other characteristic properties of the natural and inactive varieties of corydaline and of methylcorydaline.

Dehydrocorydaline hydrogen hexasulphide, $(C_{22}H_{23}NO_4)_2H_2S_6$, obtained by the action of ammonium sulphide on dehydrocorydaline hydriodide, forms small, brown, glistening needles, and behaves like berberine and strychnine hexasulphides on treatment with mineral acids.

The action of bromine on an alcoholic solution of corydaline gives rise to a *perbromide* of dehydrocorydaline hydrobromide, $C_{22}H_{23}NO_4,HBr,Br_2$, which, on boiling with alcohol, loses bromine, and is converted into dehydrocorydaline hydrobromide.

Dobbie and Lauder (Trans., 1894, **65**, 57), by the action of potassium permanganate on corydaline, obtained a substance which they called corydalinic acid. The author has been unable to corroborate this result, and could only obtain hemipinic acid; the existence of corydalinic acid is therefore doubtful. A. W. C.

The Alkaloids of Macleya cordata R. Br. By K. Hopfgartner (*Monatsh.*, 1898, 179—210).—The extract obtained from the stem and leaves of *Macleya cordata* contains two alkaloids, macleyine or protopine and β-homochelidonine. Sanguinarine, which was found along with macleyine in the roots of this plant by Eijkman (*Rec. trav. Chim.*, **3**, 182), does not appear to occur in the leaves and stem. The substance described by Eijkman as macleyine appears to be in all respects identical with the protopine obtained by various investigators from different species of Papaveraceæ; it melts at 207°, does not contain a methoxy-group, and has the formula $C_{20}H_{19}NO_5$, whereas the protopine from *Chelidonium* (König) and that from *Sanguinaria* (Tietz and König) have, according to these authors, the formula $C_{20}H_{17}NO_5$. With methylic iodide, it yields a *methiodide*, $C_{20}H_{19}NO_5,MeI$, which crystallises in thick, compact prisms, and gives a strongly alkaline solution when treated with silver oxide. The corresponding *metho-nitrate*, $C_{20}H_{19}NO_5,MeNO_3$, crystallises in white, silky needles. Potassium permanganate readily attacks protopine in

acid solution, but the only product which could be isolated was formic acid. On reduction with sodium amalgam, the alkaloid yields a *substance* which crystallises in colourless four-sided tablets, has an alkaline reaction, melts at 148°, and yields a violet-red coloration with sulphuric acid which passes into blue. The formula is probably $C_{18}H_{21}NO_4$, but has not been definitely ascertained.

The second alkaloid, the nitrate of which is much more readily soluble than that of protopine, is identical in properties with the β-homochelidonine which was obtained by Selle from *Chelidonium majus* (Abstr., 1891, 229). This base has the formula $C_{21}H_{23}NO_5$ (Selle gives $C_{21}H_{21}NO_5$), and melts at 157—158°, but when kept at this temperature for some time it solidifies again, and then melts at 166—167°. The *nitrate*, $C_{21}H_{23}NO_5,HNO_3 + 1\frac{1}{2}H_2O$, crystallises in spherical groups of needles, and the *hydrochloride*, $C_{21}H_{23}NO_5,HCl + 1\frac{1}{2}H_2O$, in slender, white needles, which are only moderately soluble in cold water. The platinochloride has not been obtained in the crystalline state, but the *hydrobromide*, $C_{21}H_{23}NO_5,HBr + 1\frac{1}{2}H_2O$, closely resembles the hydrochloride, and the *hydriodide*, $C_{21}H_{23}NO_5,HI + H_2O$, crystallises in small, white needles. A. H.

Presence of an Alkaloid in Natural Wines. By GABRIEL GUÉRIN (*J. Pharm.*, 1898, [vi], 7, 323—324).—A number of natural wines contain a small quantity of a substance of alkaloidal nature, which is probably identical with that described by Oser as formed during the fermentation of sugar by yeast (*Bull. Soc. Chim.*, 1868, [i], 10, 295.
J. J. S.

Gelatinous Matter (Pectin) in Gentian Root. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 7, 473—479. Compare Poumarède and Figuier, *ibid.*, 1847, [iii], 12, 81).—The gelatinous matter cannot be extracted by cold water, either from the dried or from the fresh root; water at 70—100°, however, dissolves out the gelatinous matter in a hydrated form (pectin); boiling 80 per cent. alcohol also serves to render the gelatinous matter soluble in water. A 1 per cent. solution of the pectin is gelatinised by a solution of pectase within 40 minutes, it is also readily gelatinised by lime water, or by the addition of sodium hydroxide followed by hydrochloric acid. Lead acetate, basic lead acetate, or ferric chloride bring about the same result. The solution yields no precipitate when saturated with sodium sulphate, but is precipitated by magnesium or ammonium sulphate. It has no reducing properties, but is dextrogyrate; $[\alpha]_D = +82 \cdot 3°$. Acidified water at 80° also extracts a pectin which is partly soluble in water, and which is more dextrorotatory than the one mentioned above; $[\alpha]_D = +145 \cdot 3°$. J. J. S.

Hepatic Pigments in Vertebrates. By A. DASTRE and N. FLORESCO (*Compt. rend.*, 1898, 126, 1221—1223).—Two pigments, for which the names *ferrin* and *cholechrome* are proposed, were extracted by various methods from fresh liver which had been freed from blood. Ferrin is a ferruginous albuminoid compound closely connected with the ferratin of Marfori and Schmiedeberg. It is readily soluble in

water and in dilute acids and alkalis, but insoluble in alcohol and chloroform. Cholechrome, on the other hand, is soluble in chloroform, but insoluble in water; it is intermediate in character between the lipochromes and biliary pigments. The absorption spectra of these pigments show no definite bands. N. L.

Decomposition of Elastin by Hydrochloric Acid. By EBBE BERGH (*Zeit. physiol. Chem.*, 1898, **25**, 337—343; SVEN G. HEDIN, *ibid.*, 344—349).—Elastin was prepared from *ligamentum nuchæ*, and from the aorta; elementary analysis of several preparations, given in full, shows that it contains sulphur. On decomposition with hydrochloric acid, it yields neither lysine nor arginine.

Hedin's paper is confirmatory of the foregoing; histidine is also absent from the products. If Kossel's recent classification of the proteids be accepted, a new class must be provided for elastin.

W. D. H.

Action of Peptic Digestion on Proteids. By F. UMBER (*Zeit. physiol. Chem.*, 1898, **25**, 258—282).—The majority of previous observers have investigated the action of pepsin-hydrochloric acid on impure proteids like fibrin. In the present research, crystalline egg-albumin, crystalline serum-albumin, and serum-globulin were employed. Attempts to crystallise serum-globulin failed; the material was prepared from blood-plasma after separation of the fibrinogen by half saturation with ammonium sulphate. In separating out the products of digestion, Pick's method of fractional precipitation with ammonium sulphate was used. Fraction 1 contained the primary proteoses; fractions 2, 3, and 4 contained three varieties of deuteroproteose, A, B, and C respectively. The peptone remaining in solution was precipitated by iodine; the iodine compound is partly insoluble in alcohol (peptone A), and partly soluble (peptone B).

The reactions of each are described, the test for sulphur, Millon's reaction, the xanthoproteic reaction, and Molisch's reaction being principally used. All the substances except peptone B gave Molisch's reaction, which is considered to indicate the existence of a carbohydrate radicle in the proteid. In all cases, too, with the exception of the two peptones, the test for loosely combined sulphur was positive. W. D. H.

Decomposition of Proteid from Conifer Seeds. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1898, **25**, 360—362).—Previous work has shown that the proteid matter from the seeds of the fir and pine yields about 10 per cent. of arginine. This is extremely high; Hedin obtained only 2·75 per cent. of this base from conglutin, and less from other proteids.

It was considered desirable to repeat this; the proteid was prepared from fir seeds by extraction with 10 per cent. solution of sodium chloride, instead of the dilute alkali previously employed. It contains 18·69 per cent. of nitrogen; this number is high; on decomposition, the amount of bases obtained exceeded that previously recorded; in fact, 34·7 per cent. of the nitrogen was obtained in the form of organic bases precipitable by phosphotungstic acid. W. D. H.

Halogen Derivatives of Albumin. By F. BLUM and WILHELM VAUBEL (*J. pr. Chem.*, 1898, [ii], 57, 365—396).—Proteids have an especial affinity for the halogen elements: for example, egg-albumin reacts with a halogen as soon as the two are brought into contact, an intramolecular substituted proteid being produced, along with considerable amounts of a halogen acid; by removing the latter, the proteid is rendered capable of undergoing further substitution, and if the reaction takes place in neutral solution, compounds are finally produced containing a constant and definite amount of halogen.

The method of procedure is, roughly, as follows. The purified albumin is heated with iodine in sodium hydrogen carbonate solution at a temperature of 50° for 4—5 hours, and the excess of iodine is then removed by shaking with sodium hydroxide solution. Egg-albumin, casein, myosin, "somatose," nuclein, and an iodised proteid derived from the thyroid gland were treated in this manner, the products obtained being for the most part tasteless and odourless yellow powders, insoluble in water and absolute alcohol, and containing from 6—7 per cent. of iodine. They did not give Millon's reaction, but did give the biuret reaction.

Bromination and chlorination may be carried out in a similar manner. The brominated egg-albumin and casein derivatives are colourless, or grey-brown, tasteless substances, containing 4—5 per cent. of bromine; the corresponding chlorine derivatives are also tasteless and colourless or brownish compounds, containing about 2 per cent. of chlorine.

The halogens may also be introduced into proteids by means of the electric current, and this is especially useful in the case of fluorine, where substitution takes place on electrolysing a solution of egg-albumin in ammonium fluoride.

When a proteid is treated with alkali, it is decomposed into (*a*) principally a basic portion containing ash; (*b*) a portion precipitated by acids, which gives both Millon's and the biuret reactions; (*c*) a portion precipitated by alcohol, giving Millon's reaction markedly and the biuret action feebly; and (*d*) a portion soluble in absolute alcohol, containing a high percentage of sulphur and smelling like mustard oil, and this also gives the biuret reaction. The halogen proteids are decomposed in a similar manner, the same products being obtained when the halogen compounds are heated with alkalis, or when the proteid is first decomposed, and the products treated with a halogen in the manner already described.

On comparing the properties of the original and decomposed products, it is noticed that the percentage of oxygen and the acid character increases in the latter, whereas the amount of sulphur decreases, and this element may be entirely absent. The amounts of carbon, hydrogen, and nitrogen remain about the same, but the percentage of halogen in the decomposition products is almost twice as great as in the original substance; this fact affords a means of determining the amount of decomposition that has taken place. Whereas the original substances are tasteless and insoluble in water and alcohol, the products of decomposition have a slightly bitter taste, and are easily soluble in 80 per cent. alcohol.

From an investigation of a large number of substituted phenol derivatives with regard to their capability of giving Millon's reaction, the authors conclude that at least two halogen atoms enter the albumin molecule, and occupy the ortho-positions relatively to the hydroxyl-group of that benzene ring, which, on decomposition, forms tyrosine. No halogen enters the other rings of the albumin molecule.

It appears, also, that there are two groups in the albumin molecule capable of producing the biuret reaction, the activity of one of these groups being destroyed during the action of a halogen.

The relation of the molecular weights of the different proteids to their products of decomposition may be obtained by preparing the fully substituted halogen products, since the capability of combining with the halogens increases with the amount of decomposition. Presuming that two halogen atoms enter the molecule of albumin, the following molecular weights are obtained. Egg-albumin and casein = 3600; myosin = 2300; nuclein = 3600; albumoses, peptones, and other decomposition products = 1700—2540.

In conclusion, the authors point out that reactions similar to the above must take place in living organisms, halogenised proteids appearing as intermediate or final products. Experiments made with "iod-," "brom-," and "chloralbacid" show that whenever a halogen is free in the organism, halogen acids and halogenised proteids are formed, to be again decomposed as soon as they come in contact with the oxidising agents of the organism, and, therefore, such compounds have a particular physiological and therapeutical interest as halogen carriers.

A. W. C.

Behaviour of Vitellin in Magnesia Mixture. By Waclaw von Moraczewski (*Zeit. physiol. Chem.*, 1898, **25**, 252—255).—The author has previously shown that in an ammoniacal solution of magnesium chloride, casein free from ash is deposited after some weeks in globules, which later become aggregations of needles. The small amounts of crystals obtained precluded a thorough examination of their composition; they, however, are believed to consist of the proteid in question. It is now shown that the similar proteid vitellin prepared from egg-yolk behaves in the same way; there is a considerable amount of amorphous admixture, but as in the case of casein, the thorough examination of the crystals has still to be made.

W. D. H.

Albumoses. By Hugo Schrötter (*Monatsh.*, 1898, **19**, 211—222).—The two albumoses of Witte's peptone, which differ in the amounts of sulphur they contain, are only imperfectly separated by means of the hydrochlorides, acetyl, and benzoyl derivatives. With a view to obtain derivatives which might facilitate the separation, the author has studied the action of nitrous acid on this peptone. An aqueous solution containing equal weights of Witte's peptone and sodium nitrite, acidified with dilute sulphuric acid, evolves nitrogen and nitrous oxides, and deposits a pale yellow substance which is dissolved by alkalis and decomposes carbonates. The new *acid* is soluble in 60 per cent. alcohol, and crystallises from this solvent on cooling, but when boiled for a long time with dilute alcohol, it becomes insoluble,

although if then dissolved by an alkali and reprecipitated by an acid, its original solubility is regained. Analysis of the acid gave results which correspond closely with the formula $C_{108}H_{140}N_{28}O_{43}S$; its *barium* salt, which separates from an aqueous solution on the addition of alcohol, has the formula $C_{108}H_{136}N_{28}O_{43}SBa_2$. In many of its properties, the acid resembles the "oxyprotosulphonic acid" obtained by Maly on oxidising unpeptonised egg-albumin with potassium permanganate (Abstr., 1885, 824), but the two are not identical. The author is unable to obtain an insoluble acid by the oxidation of Witte's peptone; moreover, by further oxidation of oxyprotosulphonic acid, Maly produced peroxyprotoic acid (Abstr., 1888, 1120), which is not formed by oxidising the author's acid. The latter substance is derived from the albumose containing the higher percentage of sulphur; it gives no nitroso-reaction, and differs therein from the acid obtained by Paal from peptone hydrochloride and silver nitrite, which is a true nitroso-compound. On the other hand, the new acid resembles Schiff's desamidoalbumin in giving neither the biuret nor the nitroso-reactions, and differs from it in decomposing carbonates. The author, in reply to some observations by Fränkel and Pick, justifies his definition of albumoses as products of the transformation of egg-albumin which, besides possessing reactions in common with peptones, also contain sulphur (compare this vol., i, 502). G. T. M.

Antipeptone. By Fr. Kutscher (*Zeit. physiol. Chem.*, 1898, **25**, 195—201).—Antipeptone was separated by Kühne from the products of pancreatic digestion by means of such reagents as ammonium sulphate and trichloracetic acid, which would free it from the amido-acids leucine and tyrosine, but not from the hexone bases, which might be formed during digestion. Hedin has previously shown that lysine is formed by tryptic activity; the present research shows that lysine, histidine, and arginine are contained mixed with the antipeptone as prepared from fibrin by Kühne, Chittenden, and Neumeister.

W. D. H.

Histon in the Urine. By Adolf Jolles (*Zeit. physiol. Chem.*, 1898, **25**, 236—241).—True peptone does not occur in urine; albumosuria is a more correct term than peptonuria. The difficulty of detecting this substance is increased by the fact that urobilin is precipitable by ammonia sulphate, and gives the biuret reaction. The author has previously shown that, in some of these cases, the proteid present is histon, which, although it is peptone-like, differs from other proteids in being precipitable from acid solutions by ammonia; it is also coagulable by heat. The cases are of pyogenic origin. The urine is freed from albumin and acidified with acetic acid; barium chloride is then added until no further precipitation takes place, this precipitate is collected, and after it has been allowed to remain several hours in contact with 1 per cent. hydrochloric acid, solid sodium carbonate is added until litmus paper is turned blue, and the liquid is filtered. The filtrate is then divided into two parts; with one portion the biuret reaction is performed, the other is acidified with dilute hydrochloric acid, and ammonia added; a precipitate indicates histon.

W. D. H.

Iodothyrin. By Ernst Roos (*Zeit. physiol. Chem.*, 1898, **25**, 242—251).—Baumann and others showed that the administration of iodine or iodine compounds increased the amount of iodine in the thyroid. The question whether the same can be done with the gland after removal from the body has hitherto remained unanswered. Potassium iodide and iodic acid were digested with thyroid gland and with iodothyrin. By this means, substances containing a large amount of iodine were obtained. These materials, however, are physiologically inactive. The method of artificial iodising therefore is quite a different one from that which leads to the formation of iodine compounds in the thyroid during life. W. D. H.

Presence of Emulsin in Lichens. By Henri Hérissey (*J. Pharm.*, 1898, [vi], 7, 577—580).—The following lichens have been found to contain emulsin: *Cladonia pyxidata* (Ach.), *Evernia furfuracea* (Ach.), *Parmelia caperata* (D. C.), *Peltigera canina* (Ach.), *Pertusaria amara* (Nyl.), *Physcia ciliaris* (D. C.), *Ramalina fastigiata* (Pers.), *R. fraxinea* (L.), and *Usnea barbata* (L.). The enzyme was detected by placing a given quantity of the pounded lichen in contact with a solution of 0·2 gram of amygdalin in 20 c.c. of water saturated with thymol. After being kept at 35° overnight, a portion of the liquid was distilled, and the distillate tested for hydrogen cyanide. J. J. S.

Action of Pepsin and Trypsin on Protamines. By Albrecht Kossel and Albert Mathews (*Zeit. physiol. Chem.*, 1898, **25**, 190—194).—Protamines (salmin and sturin) are not altered by pepsin, but they are attacked by trypsin. After the action of trypsin, protamine loses its power of precipitating albumin, and gives a red instead of a violet reaction with copper sulphate and sodium hydroxide. The substances into which protamine is changed are called protones; these are, by the prolonged action of pancreatic juice, partially broken up into hexones (lysine, histidine, arginine). There also appear to be substances intermediate between protones and hexones. The analogy between the action of trypsin on protamines (regarding them as simple proteids), and that of diastase on starch is pointed out. The fact that so large a quantity of protone resists decomposition into hexones points to the existence of an anti-group in Kühne's sense. W. D. H.

Production of Mucin by a Fluorescent Pathogenic Bacterium. By Charles Lepierre (*Compt. rend.*, 1898, **126**, 761—762).—The author's previous researches have shown that a certain fluorescent bacillus produces considerable quantities of mucin when it grows in peptone culture fluids without beef. In presence of lactates, malonates, malates, tartronates, isosuccinates, pyrotartrates, ethylmalonates, glycerates, or glycollates, the mucin is produced without any fluorescence, whereas with citrates, succinates, hydroxyglutarates, hydroxypyrotartrates, and glutarates, both mucin and the fluorescent product are formed. The mucin also forms in presence of asparagine. It contains no phosphorus, and with acids yields a reducing sugar; it is, therefore, a true mucin.

The formation of mucinoid substances has also been observed in the culture-fluids of a bacillus which the authors have described as the pathogenic organism in "sleeping sickness." C. H. B.

Organic Chemistry.

A Crystalline Compound of Acetylene with Cuprous Chloride. By R. Chavastelon (*Compt. rend.*, 1898, **126**, 1810—1812).—When cuprous acetylide is treated with hydrochloric acid in the cold, there is no appreciable evolution of gas, a fact which is attributed to the formation of a compound of acetylene with cuprous chloride, which is decomposed on warming. This compound, which analysis shows to have the composition C_2H_2,Cu_2Cl_2, may be prepared (1) by passing acetylene into a saturated solution of cuprous chloride in dilute hydrochloric acid ($HCl + 10H_2O$ to $HCl + 7H_2O$) maintained at a temperature not exceeding 12°; (2) by the action of acetylene on an aqueous or alcoholic solution of cupric chloride (20—40 per cent.) in presence of metallic copper. By the first, and most suitable, method, the substance is obtained in the form of large, hexagonal prisms belonging to the orthorhombic system, and by the second in silky needles, which are liable to contamination by a violet-purple deposit which is produced at the commencement of the reaction. In order to isolate the crystals unchanged, they must be quickly washed with absolute alcohol and anhydrous ether, both of these liquids having been previously cooled to 0° and saturated with acetylene, and finally dried in a current of acetylene. The crystals soon alter by exposure to air, and are immediately decomposed by water, or solutions of alkali chlorides, with evolution of acetylene and production of the violet-purple substance above mentioned, the nature of which is being investigated. On warming, they dissociate without explosion, and the following measurements of the pressure at different temperatures were made.

Temperature.	Pressure.	Temperature.	Pressure.
0°	3 mm.	46°	220 mm.
20	25 „	60	480 „
30	50 „	78	2620 „
40	131 „		

The compound described above is different from that prepared by Hofmann and Küspert (Abstr., 1897, i, 546), which the author was unable to obtain. N. L.

Action of Chlorine on Ethylenic Chloride in Presence of Aluminium Chloride. Chlorination of Acetylene. By A. Mouneyrat (*Compt. rend.*, 1898, **126**, 1805—1808).—When a mixture of dry ethylenic chloride with anhydrous powdered aluminium chloride is heated in a reflux apparatus at 70—75°, there is an abundant evolution of hydrogen chloride and acetylene. On passing dry chlorine into the heated mixture as long as the gas is absorbed, and subsequently pouring the liquid into hydrochloric acid, a blackish oil is

obtained which, on fractional distillation, yields some unaltered ethylenic chloride, unsymmetrical tetrachlorethane, and acetylene tetrachloride, the last-named being evidently formed by the action of chlorine on the acetylene first produced. Since, however, acetylene and chlorine unite with explosive violence under ordinary conditions, whilst no explosion took place in the experiment described, some further explanation of the reaction appeared to be necessary. In order to furnish this, a number of experiments were made, which showed that the explosion usually occurring is due to the presence of oxygen. In the absence of oxygen, chlorine and acetylene unite without explosion to form acetylene tetrachloride.

The chlorinating action of aluminium chloride appears to depend rather on the temperature at which the reaction takes place than on the amount of the reagent employed. Thus, for example, when chlorine is passed into a mixture of acetylene tetrachloride with aluminium chloride at 100°, the halogen is scarcely, if at all, absorbed; at 118—120°, however, it is rapidly absorbed, and hexachlorethane is formed. If acetylene tetrachloride is treated with bromine at 105° in presence of aluminium chloride, dichlorodibromethane, $CHClBr\cdot CHClBr$, and trichlorotribromethane are produced. The latter probably has the constitution $CCl_2Br\cdot CBr_2Cl$. N. L.

Formation of Methanedisulphonic Acid by the Action of Acetylene on Fuming Sulphuric Acid. By WILHELM MUTHMANN (*Ber.*, 1898, 31, 1880—1884).—When a current of dry acetylene gas is passed for $1\frac{1}{2}$ hours into commercial "80 per cent." fuming sulphuric acid, contained in a vessel immersed in ice and water, the acid gets very hot, sulphurous and carbonic anhydrides are evolved (but no carbonic oxide), and methanedisulphonic acid is formed. The reaction probably takes place in two stages, represented by the equations (1) $CH{:}CH + 2H_2SO_4 = CH(OH)_2\cdot CH(SO_3H)_2$;
(2) $CH(OH)_2\cdot CH(SO_3H)_2 + SO_3 = CH_2(SO_3H)_2 + CO_2 + SO_2 + H_2O$.
The barium salt, with $2H_2O$, is rhombic [$a:b:c = 0.8946:1:1.5962$]; the potassium [$a:b:c = 1.617:1:0.9367$; $\beta = 90°\ 12'$] and ammonium [$a:b:c = 1.6377:1:0.96964$; $\beta = 91°\ 42'$] salts are monoclinic, and exhibit a remarkable isomorphism with the corresponding salts of imidodisulphonic acid, $NH(SO_3H)_2$. C. F. B.

Action of Acetylene on Fuming Sulphuric Acid. By GEORG SCHROETER (*Ber.*, 1898, 31, 2189—2190. Compare Muthmann, preceding abstract).—The author claims priority over Muthmann, as he has already published a brief account of his results in Richter-Anschütz's *Lehrbuch* (1897) as follows. "Methionic acid (methane disulphonic acid) is best obtained by saturating fuming sulphuric acid with acetylene, it probably results from the decomposition of an intermediate acetaldehydedisulphonic acid." It is now shown that the formation of methionic acid can be reduced to a minimum, in this case, the chief product is acetaldehydedisulphonic acid (disulphoacetaldehyde), $CHO\cdot CH(SO_3H)_2$, together with its sulphates, for example, $SO_4H\cdot CH(OH)\cdot CH(SO_3H)_2$, which, when decomposed with hydrochloric acid, also yields disulphoacetaldehyde.

Salts of the disulphonic acid, also the phenylhydrazone, azine, and oxime have been prepared.

When boiled with alkalis, the disulphonic acid is quantitatively decomposed into salts of methionic and formic acids.

The author cannot confirm Berthelot's statement that acetylene reacts with sulphuric acid yielding acetylenesulphuric acid which, when fused with potash, gives phenol. J. J. S.

Synthesis of Potassium Carbonylferrocyanide. By JOSEPH A. MULLER (*Compt. rend.*, 1898, **126**, 1421—1423).—Potassium carbonylferrocyanide, $K_3(CO)FeC_5N_5$, is readily obtained by heating a solution of potassium ferrocyanide in an atmosphere of carbonic oxide, ammonia and potassium formate being simultaneously produced. The reaction takes place rapidly at 100°, and is completed within 48 hours at 130°. A number of analyses shows that the change occurs strictly according to the equation $K_4FeC_6N_6 + CO + 2H_2O = K_3(CO)FeC_5N_5 + NH_3 + H\cdot COOK$. N. L.

Some New Ruthenocyanides and the Double Ferrocyanide of Barium and Potassium. By JAMES L. HOWE and EDWARD D. CAMPBELL (*J. Amer. Chem. Soc.*, 1898, **20**, 29—34).—*Strontium ruthenocyanide*, $Sr_2RuC_6N_6 + 15H_2O$, is prepared by treating lead ruthenocyanide with sulphuric acid, and then neutralising with strontium hydroxide, or, in an impure state, by the action of strontium hydroxide on "Prussian purple," the ruthenium analogue of Prussian blue; it crystallises in pale straw-coloured, elongated plates, is very efflorescent, and very soluble in water; on adding alcohol to its hot aqueous solution, it crystallises in long, slender needles.

Barium potassium ruthenocyanide, $K_2BaRuC_6N_6 + 3H_2O$, is prepared by mixing solutions of the barium and potassium salts. By the action of barium hydroxide on Prussian purple, the salt is obtained mixed with the barium salt. The pure substance crystallises from its hot aqueous solution in pale amber or colourless rhombohedra very soluble in water; crystallographically it closely resembles the corresponding ferrocyanide.

Barium cæsium ruthenocyanide, $Cs_2BaRuC_6N_6 + 3H_2O$, is prepared by mixing a solution of barium ruthenocyanide with half its equivalent of cæsium sulphate, when brilliant, yellowish-white to colourless crystals separate, which, under the microscope, appear to be rhombohedra, closely resembling those of the barium potassium salt; it is insoluble even in hot water, and cannot be recrystallised, as it decomposes and forms a blue insoluble substance, which is probably ruthenium cyanide.

The magnesium, sodium, and calcium salts are very soluble and difficult to crystallise; the first forms very pale green, efflorescent crystals. *Strontium potassium* and *strontium cæsium ruthenocyanide* seem to resemble the barium double salts under the microscope, and not Wyrouboff's potassium strontium ruthenocyanide (*Ann. chim. phys.*, [iv], 21, 279). Strontium rubidium ruthenocyanide, like strontium potassium ferrocyanide, gives a precipitate when its solution is warmed.

The authors find that potassium barium ferrocyanide prepared by

mixing solutions of the barium and potassium salts, crystallises in pale, straw-coloured rhombohedra. This salt, contrary to the statement of Wyrouboff (*loc. cit.*) is perfectly stable, remaining clear and bright on prolonged exposure to air, and it crystallises, moreover, with $3H_2O$.

Barium cæsium ferrocyanide, $Cs_2BaFeC_6N_6 + 3H_2O$, obtained by decomposing barium ferrocyanide with half the equivalent of cæsium sulphate in very dilute solution, crystallises in very small, yellowish-white rhombohedra, and is sparingly soluble in water. Its hot solution appears to be stable. E. W. W.

Aliphatic Nitroso-compounds (Nitroso- and Nitro-isobutyronitrile. By OSCAR PILOTY (*Ber.*, 1898, **31**, 1878—1880).—A preliminary notice. Hydroxylamidoisobutyronitrile, $CMe_2 \cdot C(NH \cdot OH) \cdot CN$ (von Miller and Plöchl, Abstr., 1892, 1196; 1893, i, 502), can be oxidised to *nitrosoisobutyronitrile*, $CMe_2 \cdot C(NO) \cdot CN$, which is colourless, and melts and begins to decompose at 53°, yielding a blue liquid. If the oxidation is continued until the blue tint of the solution has disappeared, *nitroisobutyronitrile*, $CMe_2 \cdot C(NO_2) \cdot CN$, is obtained; this melts at 35°, and boils at 97° under a pressure of about 45 mm.; hydrolysis with strong hydrochloric acid converts it into a substance that melts and decomposes at 110—112°.

The ready conversion of the $NH \cdot OH$ group into NO or NO_2 is characteristic of its presence in direct union with a *tertiary* carbon atom (this vol., i, 223). C. F. B.

Action of Charcoal in the Purification of Spirit. By MAXIMILIAN GLASENAPP (*Zeit. angw. Chem.*, 1898, 617—621; 665—672).—The author has made an exhaustive investigation as to the part which charcoal plays in the purification of spirit, and tabulated his results. The fusel oil was estimated by Rose's process, the free acids by titration with N/20 soda, the ethers by saponification, and the aldehydes colorimetrically by means of "rosaniline bisulphite."

From the experiments, it appears that charcoal does not absorb fusel oil, but acts chemically through the oxygen condensed in its pores. The fusel oil is oxidised to ketones and aldehydes, and the latter partially to acids, which then to some extent act on the alcohols, forming ethereal salts (compound ethers), these various mixed products causing a characteristic odour and taste. They are soluble in chloroform, and unless previously removed they would count as fusel oil in Rose's well-known process.

Charcoal absorbs these products to a large extent; in fact, filtered spirit often shows less aldehydes than the unfiltered sample. If the charcoal is afterwards heated to regenerate it, the spirit thus obtained is rich in ethers and aldehydes, but does not contain more fusel oil than the original liquor. The author advises treating the regenerated charcoal in a current of dry air so as to thoroughly impregnate it with oxygen. It is thought probable that a better product might be obtained by filtering the spirit at a somewhat higher temperature than usual. L. DE K.

Monalkyl-phosphoric Acids. By JACQUES CAVALIER (*Compt. rend.*, 1898, **126**, 1285—1287).—The monethylphosphates are very

stable in solution, and are much less readily decomposed by alkalis than is the acid itself by water. In dilute solutions, there is practically no hydrolysis in presence of excess of alkali. The values obtained by the author for the heat developed by the addition of a third equivalent of a base (this vol., ii, 499) are markedly lower than the value given by Belugou (this vol., ii, 498), but agree with the corresponding value obtained by Imbert and Belugou in the case of glycerophosphoric acid. The normal salts of ethylphosphoric acid are but slightly dissociated in aqueous solution, a result which is confirmed by the sharpness of the end reaction with phenolphthalein. C. H. B.

Psyllostearylic Alcohol. By ERNST E. SUNDVICK (*Zeit. physiol. Chem.*, 1898, **25**, 116).—A molecular weight determination by Beckmann's method, using chloroform as solvent, of the substance formerly described as psyllostearylic alcohol (Abstr., 1893, i, 125), shows that it has the formula $C_{66}H_{132}O_2$ instead of $C_{33}H_{66}O$. When heated with hydrobromic acid (sp. gr. = 1·49) during three-quarters of an hour at 210—220°, it yields a product which contains no bromine (compare *loc. cit.*), and appears to be a diatomic *alcohol*, $C_{33}H_{66}(OH)_2$; to this substance, the author has transferred the name *psyllostearylic alcohol*, the product formerly so named apparently being the *ether*, $\begin{array}{l}C_{33}H_{66}\text{—}O\\ |\qquad\quad\ \ |\\ O\text{———}C_{33}H_{66}\end{array}$. The new substance crystallises from benzene in beautiful rhombs having an angle of 74°, and melts at 86—87° (uncorr.) after its water of crystallisation has been expelled. The latter is retained very tenaciously; the crystals obtained from light petroleum contain $13H_2O$, and after being kept 2 months in a desiccator over sulphuric acid, still retain $3H_2O$; the crystals from chloroform contain $11H_2O$, and those from benzene $10H_2O$. W. A. D.

Dimethylheptenol, a New Unsaturated Tertiary Alcohol. By PHILLIPE BARBIER (*Compt. rend.*, 1898, **126**, 1423—1426).—When lemonol (200 grams) is heated for 8 hours at 150° with potassium hydroxide (100 grams) dissolved in a little alcohol, and the product treated with water, a colourless oily liquid separates which, after rectification, boils at 79° under a pressure of 10 mm. This is shown by analysis to have the composition $C_9H_{18}O$, and since, on oxidation with chromic acid mixture, it yields methylheptenone together with small quantities of acetone and levulinic acid, it must be 2 : 6-*dimethyl-2-heptene-6-ol*, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$. The *acetate*, obtained by the action of acetic anhydride at 140°, is a liquid of agreeable aromatic odour boiling at 84—86° under a pressure of 11 mm. When dimethylheptenol is agitated for some hours with 50 per cent. sulphuric acid in the cold, it takes up a molecule of water and forms the ditertiary *glycol*, $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$. The latter, being unstable, readily loses water and yields *dimethylheptene oxide*, a colourless, mobile liquid boiling at 132—133°, and having a strong odour of mint and camphor. It probably has the constitution $CH_2{<}{\begin{array}{l}CH_2{\cdot}CMe_2\\CH_2{\cdot}CMe_2\end{array}}{>}O$. N. L.

Separation of Geraniol from Citronellol. By JULIAN FLATAU and H. LABBÉ (*Compt. rend.*, 1898, **126**, 1725—1727).—The process devised by the authors for the separation of geraniol from citronellol is based upon the difference in the solubilities of the phthalates in light petroleum. The mixture of the two alcohols is boiled, in a reflux apparatus, with its own weight of phthalic anhydride dissolved in benzene, and the ethereal salts thus obtained are, after purification, dissolved in light petroleum at 20—25°. On cooling the solution to $-5°$, geranyl phthalate separates in the crystalline form, whilst by evaporating the remaining liquid citronellol phthalate is obtained as an uncrystallisable yellow oil. The results are given of the examination by this method of separation of a number of specimens of essence of geranium, essence of roses, &c.

Geraniol was obtained as a colourless liquid of agreeable rose-like odour, boiling at 228·2° under a pressure of 750 mm., and having a sp. gr. = 0·8965 at 0°. Citronellol boils at 221·5° under a pressure of 755 mm., and has an odour resembling both rose and geranium. *Geranyl phthalate*, $CMe_2\!:\!CH\cdot CH_2\cdot CH_2\cdot CMe\!:\!CH\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot COOH$, crystallises in rhombic tablets melting at 47°, and is readily soluble in most organic solvents in the cold, with the exception of light petroleum. When treated with the theoretical amount of bromine in ethereal solution, it yields *tetrabromogeranyl phthalate*,

$CMe_2Br\cdot CHBr\cdot CH_2\cdot CH_2\cdot CMeBr\cdot CHBr\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot COOH$,

which, after recrystallisation from light petroleum, melts at 114—115°. The following ethereal salts were prepared by heating citronellol or geraniol with excess of acid in sealed tubes at 150—160° in presence of anhydrous cadmium acetate; the figures represent boiling points under a pressure of 30—35 mm. *Citronellol acetate*, 172—173°; *citronellol valerate*, 194—196°; *citronellol hexoate* (from active hexoic acid), 168—170°; *citronellol crotonate*, 138—140°; *geraniol valerate*, 130—132°. N. L.

Reaction of Tertiary Alcohols and their Ethereal Salts. By GEORGES DENIGÈS (*Compt. rend.*, 1898, **126**, 1277—1279).—When a tertiary alcohol is heated with an acid solution of mercuric sulphate (this vol., i, 549), it yields a more or less deep yellow or reddish precipitate identical in composition with the product obtained from the corresponding olefine under similar conditions (*loc. cit.*). Tertiary alcohols which do not yield olefines on dehydration do not give this reaction, neither do primary or secondary alcohols. On the other hand, it is obtained with the ethereal salts formed by the tertiary alcohols. In some cases, the precipitate rapidly oxidises if left in contact with the liquid in which it is formed. C. H. B.

Action of Sulphurous and Hyposulphurous Acids on Pure and Impure Solutions of Sugar. By L. BEAUDET (*Bied. Centr.*, 1898, **27**, 426—427; from *Bul. Assoc. Chim.*, **15**, 90).—Sulphurous acid acts very slightly on pure sugar below 50°, but acts appreciably at 55°, and very rapidly at higher temperatures. The more acid present, the greater the amount of sugar decomposed. Decomposition is much more energetic during the first 5 minutes than, for instance,

after 20 minutes. Results obtained with pure sugar do not, however, apply to syrups, &c., as even very slight amounts of impurities are sufficient to hinder the decomposition.

Hyposulphurous acid has no action either on pure or impure sugar solutions. N. H. J. M.

Maltose. By JAMES O'SULLIVAN (*J. Soc. Chem. Ind.*, 1897, **16**, 112).—Carefully purified, anhydrous maltose, prepared by acting on starch with diastase precipitated from malt extract by alcohol, has a specific rotatory power $[\alpha]_j = 155 \cdot 15$, and a cupric-reducing power $K = 63$. In determining the latter, C. O'Sullivan's method (this Journal, 1876, ii, 130) was closely followed; allowance, however, should be made, in using this method, for the cupric oxide present in the ash of the filter paper, due to the absorption of the copper solution by the cellulose during filtration; in many cases, the weight of the ash is more than doubled from this cause. W. A. D.

[NOTE BY ABSTRACTOR.—Brown, Morris and Millar (Trans., 1897, 100 and 110) have given for maltose the values $[\alpha]_j = 153 \cdot 25$ for solutions up to 20 per cent. concentration, and $K = 62 \cdot 24$].

The Carbohydrate obtained from Egg-Albumin. By OTTO WEISS (*Centralb. Physiol.*, 1898, **12**, 515—516).—The carbohydrate obtained by Pavy's method from egg-albumin (freed from ovo-mucoid) is a methylpentose, and therefore an isomeride of rhamnose ($C_6H_{12}O_5$); the pentose itself crystallises in monoclinic, colourless crystals melting at 91—93°, and is soluble in water and in alcohol. W. D. H.

A New Carbohydrate in the Liver. By JOSEF SEEGEN (*Centralb. Physiol.*, 1898, **12**, 505—515).—By extracting the liver with water, a new carbohydrate, in addition to sugar and glycogen, is obtained. It does not reduce Fehling's solution, but by prolonged heating with dilute mineral acid in a closed tube, is converted into glucose. It requires 90 per cent. of alcohol to precipitate it. By treating the liver according to the Külz-Brücke method, alcohol precipitates only a small quantity of this new substance with the glycogen.

The new substance, for which the name *liver-dextrin* is suggested, is contained in the liver in quite large quantities. W. D. H.

Nitration of Cellulose, Hydrocellulose, and Oxycellulose. By LÉO VIGNON (*Compt. rend.*, 1898, **126**, 1658—1661).—Repeated treatment of cellulose, hydrocellulose, and oxycellulose with a mixture of sulphuric and nitric acids at 10—12°, together with successive analyses of the compounds produced, showed that the final product of the reaction corresponded, in each case, with the fixation of 11 NO_2 groups by a molecule containing 24 atoms of carbon. On exposure to air, nitrohydrocellulose becomes yellow and decomposes; nitro-oxycellulose is rather more stable, whilst nitrocellulose is unaffected. The behaviour of these nitro-derivatives with Schiff's reagent, Fehling's solution, and potash show that all three possess aldehydic characters, which are most marked in the case of nitro-oxycellulose. The latter also, when distilled with hydrochloric acid, yields a larger proportion of furfuraldehyde than is obtained from nitrocellulose and nitrohydrocellulose. N. L.

Formation of Furfuraldehyde from Cellulose, Oxycellulose, and Hydrocellulose. By LÉO VIGNON (*Compt. rend.*, 1898, **126**, 1355—1358).—Hydrocellulose, oxycellulose, and reduced cellulose, the last-named being apparently identical with hydrocellulose, were obtained by treating carefully purified cotton wool (10 grams) and water (1000 c.c.) with, (1) 65 c.c. of hydrochloric acid of 22°, (2) 65 c.c. of hydrochloric acid and 80 grams of potassium chlorate, (3) 65 c.c. of hydrochloric acid and 50 grams of stannous chloride. From these and some other substances, the following percentage yields of furfuraldehyde were obtained. Hydrocellulose, 0·854; oxycellulose, 2·113; reduced cellulose, 0·860; starch, 0·800; bleached cotton, 1·800; oxycellulose, prepared by means of chromic acid, 3·500. Two specimens of oxycellulose were prepared by treating cotton wool with hydrochloric acid and potassium chlorate (A), and with sulphuric acid and potassium dichromate (B), and 25 grams of each product digested with aqueous potash of 20°. Of the product A, 16·20 grams were insoluble in potash, 2·45 grams were precipitated on neutralisation of the alkaline solution, and 6·35 grams remained in solution, whilst B yielded 11·16 grams of insoluble matter, 1·42 grams were precipitated by acid, and 12·42 grams remained in solution. The percentage yields of furfuraldehyde obtained from these fractions were as follows. A, insoluble, 0·86; precipitated, 4·35; dissolved, 1·10: B, insoluble, 0·76; precipitated, 5·11; dissolved, 1·54. It appears, from the foregoing results, that the cellulose molecule, after oxidation, is easily decomposed by potash, the insoluble and larger portion having all the characters of the original cellulose, whilst the soluble portion is of an aldehydic nature, and contains a substance, precipitable by acids, which yields a relatively large amount of furfuraldehyde. N. L.

Alkyl Bismuth Iodides, and Bismuth Iodides of Vegetable Bases. By ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1898, **20**, 96—100).—Alkylammonium iodides are capable of completely precipitating bismuth salts from solution, in the form of an orange-yellow powder; the *tetralkylammonium bismuth iodides* thus formed are slightly decomposed by water and by concentrated mineral acids, but are stable in the air at temperatures above 100°, and are not changed by treatment with potassium thiosulphate; they are sparingly soluble in ethylic and methylic alcohols, and insoluble in glacial acetic acid, ether, chloroform, and benzene. *Tetramethylammonium bismuth iodide*, $N_3Me_{11}HBi_2I_7$, crystallises from dilute hydrochloric acid.

Dragendorff's reagent gives, with pyridine salts, a dark orange-red precipitate of *pyridine bismuth iodide*, $(C_5NH_5)_3(HI)_2Bi_2I_6$, which can be crystallised from alcohol; atropine, strychnine, and brucine give *derivatives* of probably similar composition.

The author suggests constitutional formulæ as possibly representing the constitution of the above derivatives, in which iodine is assumed to be tervalent. W. A. D.

Chitosamine—Glucosamine. By ROBERT BREUER (*Ber.*, 1898, **31**, 2193—2200. Compare Tiemann, Abstr., 1884, 724; 1886, 329; 1894, i, 166; Fischer and Tiemann, *ibid.*, 1894, i, 167; Winterstein, 1896, i, 520).—Chitosamine hydrochloride can be freed from calcium sulphate

by dissolving it in 80 per cent. alcohol, and then pouring a hot concentrated aqueous solution of the purified compound into 10—15 times its volume of cold absolute alcohol, with constant stirring; 5 grams of this finely divided and dried hydrochloride is mixed with 60 c.c. of absolute alcohol and 2·5 grams of diethylamine, and the mixture left in a closed flask at the ordinary temperature for 24 hours, the crystals being treated a second, and, if necessary, a third, time in a similar manner, with the addition of a little chloroform, and finally washed with alcohol, chloroform, and a mixture of alcohol and ether in the order given. The free base, $C_6H_{13}NO_5$, is thus obtained as an extremely fine, crystalline powder, which can be recrystallised from boiling methylic alcohol; the yield is about 90 per cent. of the theoretical. The base is extremely readily soluble in water, yielding an alkaline solution; it is sparingly soluble in hot ethylic, or cold methylic alcohol, and is insoluble in chloroform or ether. When heated in a capillary tube, it turns brown at 105°, and decomposes at 110°. Its specific rotatory power $[\alpha]_D = +47·08$, or, after remaining for 18 hours, $= +48·83$; with a somewhat more dilute solution, the numbers found were 48·64 and 50·39 respectively.

In a perfectly dry state, it can be preserved over sulphuric acid for months, but, when kept in stoppered bottles, it is slowly converted into a brown mass, whilst in aqueous solution, decomposition takes place with the greatest readiness, ammonia being evolved. It is on account of the readiness with which it undergoes decomposition in the presence of water that the base has not previously been obtained in a pure form. Its aqueous solutions readily reduce alkaline, and even cold neutral, solutions of salts of the heavy metals.

The hydrobromide, $C_6H_{13}NO_5,HBr$, is obtained when concentrated hydrobromic acid is added to a solution of the base in methylic alcohol. The *hydriodide*, obtained in a similar manner, crystallises in large, colourless plates, which are soluble in water, and also in methylic and ethylic alcohols; it turns brown at 135°, and decomposes at about 165°. A crystalline *sulphate* has also been obtained. The *oxalate*, $C_{14}H_{28}N_2O_{14}$, crystallises in fine needles when a concentrated aqueous solution is precipitated with alcohol and ether; it turns brown between 145° and 150°, and melts and decomposes at 153°. The corresponding *citrate* and *tartrate* have also been prepared, but no crystalline acetate. *Monacetylchitosamine* crystallises in long, colourless needles decomposing at about 190°; it is readily soluble in water and in boiling methylic alcohol. The *oxime*, $C_6H_{14}N_2O_5$, crystallises from its solution in methylic alcohol in hard prisms, and melts at about 127°. The same oxime may be obtained when Winterstein's chitosamineoxime hydrochloride is suspended in alcohol and treated with diethylamine. The *diphenylhydrazone*, $C_{18}H_{23}N_3O_4$, can only be obtained in a crystalline form from the hydrochloride of the base under special conditions, and not from the base itself; it crystallises in long, colourless needles, is insoluble in absolute alcohol, ether, or chloroform, turns brown at 140°, and melts with decomposition at 162°. It dissolves in warm water, but undergoes decomposition at the same time. The *semicarbazone* of the *hydrochloride*, $C_7H_{17}N_4O_5Cl$, crystallises from 90 per cent. alcohol in small, colourless needles, and is

readily soluble in water, but insoluble in absolute methylic or ethylic alcohol. When heated in a capillary tube, it changes colour at 140°, and decomposes at 160—170°; when treated with diethylamine, it yields the *semicarbazone* of the free base, $C_7H_{16}N_4O_5$, which crystallises in small needles melting and decomposing at 165°. d-*Glucose semicarbazone*, $C_7H_{15}N_3O_6$, crystallises in colourless needles melting and decomposing at 175°. All three carbazones, when heated in aqueous solution with benzaldehyde, yield benzylidenesemicarbazone.

J. J. S.

Choline and its Derivatives. By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1898, **24**, 513—541).—Pure choline is probably a syrupy liquid which cannot be crystallised at the ordinary temperature; when exposed to the air, however, it becomes crystalline, owing to the formation of its carbonate by the absorption of carbonic anhydride.

Crystalline precipitates are produced in very dilute solutions of choline chloride by phosphomolybdic and phosphotungstic acids, and by iodine dissolved in potassium iodide; potassium bismuth iodide, potassium cadmium iodide, potassium mercury iodide, and mercuric and gold chlorides give precipitates with more concentrated solutions, whilst potassium zinc iodide, mercuric cyanide, platinum tetrachloride, and picric acid yield none. Brieger and others have stated that choline, unlike neurine, is not precipitated by tannin; the author finds, however, that in perfectly neutral solutions a precipitate is formed which is very soluble in acids and in alkalis; if a concentrated solution of choline chloride is employed, the hydrochloric acid produced in the reaction has to be neutralised with moist silver oxide before the precipitate will separate.

It appears that choline platinochloride, $(C_5H_{14}NOCl)_2,PtCl_4$, is polymorphous; from hot solutions, rhombic (?) crystals are obtained, which, in time, change into monosymmetric prisms; $a:b:c = 1.1439:1:0.6826$; $\beta = 85° 35\frac{1}{2}'$ (Vernadsky). The melting point of the platinochloride is not characteristic; different preparations of the pure salt melted at temperatures between 211° and 218°, whilst other investigators state that it melts at various temperatures between 225° and 241°. Hundeshagen's statement (*J. pr. Chem.*, [ii], **28**, 246) that choline platinochloride is anhydrous is confirmed (compare Babo and Hirschbrunn, *Annalen*, **84**, 25; and Jahns, Abstr., 1891, 94); 1 part of the salt dissolves in 5·82 parts of water at 21°. Choline chloride, when pure, is completely precipitated from its alcoholic solution by platinum tetrachloride, but only partially when impure. Choline aurochloride, like the platinochloride, melts at no definite temperature. The mercury double salt, $C_5H_{14}NOCl,6HgCl_2$, crystallises in rhombohedral aggregates, $a:c = 1:2.1986$, and melts at 249—251°; at 24·5°, it dissolves in 56·6 times its weight of water.

Dilute solutions of choline can be boiled with barium hydroxide, and with sodium ethoxide, without undergoing change; no neurine is formed when a solution of choline chloride is evaporated with hydrochloric acid, although it appears to be produced by the slow spontaneous decomposition of choline solutions.

W. A. D.

Alkyl Derivatives of Hydroxylamine. By ARTHUR R. HANTZSCH and W. HILLAND (*Ber.*, 1898, **31**, 2058—2067).—By the action of methylic iodide on hydroxylamine, the authors have obtained the same product as that described by Dunstan and Goulding (Trans., 1896, 839), namely, trimethylhydroxylammonium iodide, $OH\cdot NMe_3\cdot I$; for the preparation of this compound, practically the method of Dunstan and Goulding has been employed. It is readily soluble in alcohol or water, but is insoluble in ether, and gives an acid reaction, even after repeated crystallisation from alcohol. When heated, it melts and decomposes at 130°, but undergoes slow decomposition even at the ordinary temperature, and is therefore best preserved in alcoholic solution. Even when smaller quantities of methylic iodide are employed, the only product is the trimethyl derivative. *Trimethylhydroxylammonium chloride* is obtained when an aqueous solution of the iodide is digested with silver chloride until no more iodine is left in solution, the filtrate evaporated, and the residue recrystallised from hot alcohol, when the chloride is deposited as needles melting at 218° and decomposing at a slightly higher temperature. The *platinochloride*, $(OH\cdot NMe_3)_2PtCl_6 + 2H_2O$, forms rhombohedral crystals melting and decomposing at 215—216°. The *picrate* crystallises in intensely yellow needles decomposing at 197—198°. The normal *sulphate* can only be obtained in the form of a thick syrup. The *carbonate*, obtained by digesting a solution of the sulphate with an excess of barium carbonate and evaporating the filtrate in a vacuum, crystallises from its concentrated solutions in beautiful, colourless, transparent plates. *Trimethylamine oxide* can only be obtained in aqueous solution, that is, as trimethylhydroxylammonium oxide, by carefully treating the iodide with freshly precipitated silver oxide at 0°, and then rapidly filtering from the silver iodide. The base is not soluble in ether, has a strongly alkaline reaction, rapidly absorbs carbonic anhydride, and is volatile with steam, but the greater part at the same time undergoes decomposition. Solutions of the base have strong reducing properties; silver salts, Fehling's solution, and potassium iodide solutions being immediately reduced, and in all cases a strong odour of trimethylamine is observable. The addition of alkalis to the aqueous solution also causes decomposition, and it is thus probable that trimethylhydroxylammonium hydroxide is only stable when completely ionised. Trimethylamine oxide could not be obtained by the action of nitromethane on zinc methyl.

If hydroxylamine is treated with ethylic iodide, even when a large excess of the latter is employed, the product is β-ethylhydroxylamine, and not a triethyl derivative. *β-Ethylhydroxylamine hydriodide*, $OH\cdot NH_2EtI$, crystallises in prisms, melts at 75°, is extremely hygroscopic, and readily decomposes. The chloride, platinochloride, aurochloride, and picrate could only be obtained as oils. The free base is readily decomposed.

J. J. S.

Formhydroxamic Acid. By GEORG SCHROETER (*Ber.*, 1898, **31**, 2190—2192).—The author cannot confirm Nef's statement (this vol., i, 102) that formhydroxamic acid, $OH\cdot CH{:}N\cdot OH$, decomposes spontaneously at 0°. The acid was prepared and investigated some five years

ago by the author. A solution of pure hydroxylamine in methylic alcohol is mixed with the equivalent quantity of ethylic formate and allowed to remain for several days at the ordinary temperature; after distilling off the methylic alcohol under reduced pressure, the pure acid is obtained in colourless, glistening plates melting at 72—74°. It begins to decompose a few degrees above its melting point, and explodes at 80—90°; decomposition also takes place very slowly at the ordinary temperature, but the acid can be kept for several weeks in a desiccator. It dissolves readily in water or alcohol, but is insoluble in ether; its aqueous solution gives an intense red coloration with ferric chloride, whilst with ammoniacal copper sulphate, a green *copper* salt, $CH{<}{}^{NO}_{-O-}{>}Cu$, is obtained.

α-Benzylhydroxylamine, when heated with ethylic formate at 150° in sealed tubes, yields *dibenzylic formhydroxamoxime*,

$$C_7H_7O{\cdot}N{:}CH{\cdot}NH{\cdot}OC_7H_7,$$

boiling at 170° under 15 mm. pressure. When the mixture is heated to 160°, another compound boiling at 188° under 15 mm. pressure is obtained. J. J. S.

Double Salts of Organic Bases with Mercury Haloids. By Daniel Strömholm (*Ber.*, 1898, **31**, 2283—2310).—Double salts of sulphinic chlorides with mercuric chloride belong to one of five classes having the general formulæ, $2RCl + HgCl_2$, $RCl + HgCl_2$, $RCl + 2HgCl_2$, $RCl + 3HgCl_2$, and $RCl + 6HgCl_2$.

The trimethylsulphine *mercurichlorides*, $2SMe_3Cl + HgCl_2$, $SMe_3Cl + HgCl_2$, $SMe_3Cl + 2HgCl_2$, and $SMe_3Cl + 6HgCl_2$, melt at 204°, 193°, 128°, and 174° respectively. Dimethylethylsulphine *mercurichloride*, $SMe_2EtCl + HgCl_2$, melts at 117—119°; two other double salts have been described by Klinger and Maassen. Methyldiethylsulphine *mercurichloride*, $SMeEt_2Cl + HgCl_2$, sinters at 64°, and melts at 73°; two other double salts have been described by Klinger and Maassen.

The triethylsulphine *mercurichlorides*, $SEt_3Cl + HgCl_2$, $SEt_3Cl + 2HgCl_2$, and $SEt_3Cl + 6HgCl_2$, melt at 82°, 126—127°, and 189—190° respectively.

Methylethylisopropylsulphine *mercurichloride*, $SMeEtPr^{\beta}Cl + 2HgCl_2$, crystallises in elongated prisms and melts at 88·5°. The methylethylpropylsulphine *mercurichlorides*, $SMeEtPr^{\alpha}Cl + 2HgCl_2$, and

$$SMeEtPr^{\alpha}Cl + 6HgCl_2,$$

melt at 72—73° and 169° respectively.

The methylethylisobutylsulphine *mercurichlorides*, $SMeEt(C_4H_9)Cl + 2HgCl_2$, $SMeEt(C_4H_9)Cl + 3HgCl_2$, and $SMeEt(C_4H_9)Cl + 6HgCl_2$, melt at 50—51°, 77°, and 147° respectively.

Methylethylamylsulphine *mercurichloride*, $SMeEt(C_5H_{11})Cl + 2HgCl_2$, melts at 83°.

Methyldiamylsulphine *mercurichloride*, $SMe(C_5H_{11})_2Cl + 2HgCl_2$, melts at 68—70°.

Methylethylhexylsulphine *mercurichloride*, $SMeEt(C_6H_{13})Cl + 3HgCl_2$, melts at 79—80°.

The methyldi-isobutylsulphine *mercurichlorides*, $SMe(C_4H_9)_2Cl + 2HgCl_2$ and $SMe(C_4H_9)_2Cl + 6HgCl_2$, melt at 103° and 127° respectively.

Methyldipropylsulphine *mercurichloride*, $SMePr^{\alpha}{}_2Cl + 6HgCl_2$, melts at 121°, and methyldi-isopropylsulphine *mercurichloride*, $SMePr^{\beta}{}_2Cl + 6HgCl_2$, melts at 197°.

Diethylenebisulphidemethylsulphine *mercurichloride*, $SMe(C_4H_8S)Cl + 3HgCl_2$, melts at 198°. Oxydiethylenebisulphidemethylsulphine *mercurichloride*, $SMe(C_4H_8OS)Cl + 2HgCl_2$, has been analysed; the *mercurichloride*, $SMe(C_4H_8OS)Cl + 6HgCl_2$, decomposes at 230°.

Triethylsulphine *mercuribromide*, $SEt_3Br + 6HgBr_2$, melts at 169°; the *mercuricyanides*, $SEt_3Cl + 2Hg(CN)_2$ and $SEt_3CN + 2Hg(CN)_2$, melt at 100—101° and 158° respectively.

Methyldiethylsulphine *mercuricyanide*, $SMeEt_2CN + 2Hg(CN)_2$, melts at 133—136°.

Tetrethylammonium *mercuricyanide*, $NEt_4{\cdot}CN + 2Hg(CN)_2$, dissolves readily in water and in alcohol, and melts at a very high temperature.

The dimethylthetine *mercurichlorides*, $COOH{\cdot}CH_2{\cdot}SMe_2Cl + 2HgCl_2$ and $COOH{\cdot}CH_2{\cdot}SMe_2Cl + 6HgCl_2$, melt at 130° and 128° respectively. Methylethylthetine *mercurichloride*, $COOH{\cdot}CH_2{\cdot}SMeEtCl + 6HgCl_2$, and diethylthetine *mercurichloride*, $COOH{\cdot}CH_2{\cdot}SEt_2Cl + 6HgCl_2$, have been also prepared.

The *mercurichlorides*, $S{<}{\substack{CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2}}{>}SCl{\cdot}CH_2{\cdot}COO{\cdot}HgCl + 3HgCl_2$ and $O{:}S{<}{\substack{CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2}}{>}SCl{\cdot}CH_2{\cdot}COO{\cdot}HgCl + 2HgCl_2$, melt at 180° and 162° respectively.

Ethylisopropylaniline *mercurichloride*, $NEtPr^{\beta}PhCl + 4HgCl_2$, melts at 137—140°.

The foregoing salts of the type $RCl + 6HgCl_2$ are isomorphous, and crystallise in rhombohedra.

When the double salts of organic bases and mercuric chloride are agitated with ether which is not quite dry, a portion of the inorganic constituent is eliminated. The action of ether has been studied in a large number of cases, and is described in the original paper, which also contains views regarding the constitution of the double salts in question. M. O. F.

Action of Aluminium Chloride and of Chlorine in presence of Aluminium Chloride on Choral. By A. Mouneyrat (*Compt. rend.*, 1898, **126**, 1519—1522).—Combes found that when aluminium chloride and dry chloral are heated at 70°, carbon dichloride, a polymeride of chloral, and aluminium hydroxide are formed. The author finds that if the reaction takes place at 100°, the same products are obtained and also a considerable quantity of pentachlorethane. It would seem that part of the aluminium chloride acts in the same way as phosphorus pentachloride.

Direct experiment shows that when pentachlorethane is heated at 100° with aluminium chloride, it is quantitatively converted into carbon dichloride with liberation of hydrogen chloride, and it would follow that the latter is not a direct product of the action of aluminium chloride on chloral, but that pentachlorethane is first produced, probably with intermediate formation of a compound, $AlCl_2{\cdot}CCl_2{\cdot}CCl_3$, and is

afterwards converted into the dichloride by the further action of the aluminium chloride.

When a current of chlorine is passed into a mixture of pentachlorethane and aluminium chloride heated at 100°, hexachlorethane is obtained, the yield being quantitative. No doubt the chlorine combines with the carbon dichloride at the moment of its formation. Similarly, if bromine is dropped into the mixture of pentachlorethane and aluminium chloride, symmetrical tetrachlorodibromethane is obtained in large quantity. C. H. B.

Compounds of Chloral with Formaldehyde. By ADOLF PINNER (*Ber.*, 1898, **31**, 1926—1938).—*Hexachlorodimethyltetroxan*,

$$CCl_3\cdot CH<\begin{matrix}O\cdot CH_2\cdot O\\O\cdot CH_2\cdot O\end{matrix}>CH\cdot CCl_3,$$

is prepared in the following manner. Chloral hydrate (2 parts), dissolved in a 40 per cent. solution of formaldehyde (1 part), is vigorously agitated with concentrated sulphuric acid (7 parts), and cooled meanwhile by immersing the flask in cold water; the liquid separates into two layers, and deposits crystals if shaken from time to time during 2—3 days. The solid product is collected and washed with water, being subsequently extracted with ether to remove hexachlorodimethyltrioxin. It crystallises from glacial acetic acid in highly refractive, lustrous prisms, and melts at 189°; it is insoluble in water, and dissolves with difficulty in boiling alcohol and acetone, but more readily in hot benzene and petroleum. The substance volatilises above its melting point without decomposing, the pungent odour of formaldehyde becoming perceptible; it is indifferent towards acids and alkalis at common temperatures, and nascent hydrogen eliminates only two chlorine atoms.

Tetrachlorodimethyltetroxan, $CHCl_2\cdot CH<\begin{matrix}O\cdot CH_2\cdot O\\O\cdot CH_2\cdot O\end{matrix}>CH\cdot CHCl_2$, obtained on adding zinc dust to a solution of the foregoing substance in boiling glacial acetic acid, crystallises in slender, white needles, and melts at 87°.

Diethoxytetrachlorodimethyltetroxan,

$$OEt\cdot CCl_2\cdot CH<\begin{matrix}O\cdot CH_2\cdot O\\O\cdot CH_2\cdot O\end{matrix}>CH\cdot CCl_2\cdot OEt,$$

is prepared by agitating hexachlorodimethyltetroxan with alcoholic sodium ethoxide in a sealed tube at 100° during 10 hours; the solution is then diluted, neutralised with carbonic anhydride, and freed from alcohol by evaporation. It crystallises from alcohol in aggregates of lustrous prisms, and melts at 114°.

Tetrachlorodimethenetetroxan, $CCl_2{:}C<\begin{matrix}O\cdot CH_2\cdot O\\O\cdot CH_2\cdot O\end{matrix}>C{:}CCl_2$, is a byeproduct in the preparation of the foregoing substance, but is more conveniently obtained by heating hexachlorodimethyltetroxan (3 parts) with caustic potash (2 parts) and aniline (10—15 parts) in a reflux apparatus at 150—160° during 5—10 minutes; it crystallises in long, colourless needles or stout prisms, and melts at 106°. In preparing this compound, the alkali should be finely divided; if 2 parts of alkali to 1 part of the chloro-derivative are employed, a resinous

product containing oxalic acid is obtained, and the odour of isocyanide becomes perceptible.

Chloral methyleneglycoloxide, $CCl_3{\cdot}CH(OH){\cdot}O{\cdot}CH_2{\cdot}OH$, prepared by heating hexachlorodimethyltetroxan with alcoholic ammonia at 200°, separates from the liquid in brownish prisms melting at 130°; on submitting this compound to distillation in a current of steam, chloral methyleneglycoloxide is obtained in slender, white needles. It softens at 95° and slowly melts at 120°.

Hexachlorodimethyltrioxin, $CCl_3{\cdot}CH{<}\begin{matrix}O\text{———}CH_2\\O{\cdot}CH(CCl_3)\end{matrix}{>}O$, is obtained, as already mentioned, as a bye-product in the preparation of hexachlorodimethyltetroxan; it crystallises from alcohol in colourless, transparent, rhombic plates and melts at 129°.

Tetrachlorodimethyltrioxin, $CHCl_2{\cdot}CH{<}\begin{matrix}O\text{————}CH_2\\O{\cdot}CH(CHCl_2)\end{matrix}{>}O$, prepared by adding zinc dust to a solution of the foregoing substance in hot, glacial acetic acid, crystallises from the diluted liquid in lustrous needles melting at 67—68°; it slowly volatilises in the desiccator, giving rise to the penetrating odour of formaldehyde.

Tetrachlorodimethenetrioxin, $CCl_2{:}C{<}\begin{matrix}O\text{———}CH_2\\O{\cdot}C({:}CCl_2)\end{matrix}{>}O$, is formed from tetrachlorodimethyltrioxin under the influence of hot alcoholic potash; it melts at 75—79°, and gradually decomposes spontaneously, yielding a fuming liquid having the odour of phosgene.

Pentachlorodimethyltrioxin, $CCl_3{\cdot}CH{<}\begin{matrix}O\text{——}CH_2\\O{\cdot}C(CCl_2)\end{matrix}{>}O$, is prepared from hexachlorodimethyltrioxin by the action of alcoholic ammonia at 150—160°, and is separated from the product by the action of a current of steam; it crystallises in colourless leaflets, and melts at 67—69°.

The resinous product obtained in the preparation of chloral methyleneglycollate is probably *dichloral methyleneglycoloxide*,

$$CH_2[O{\cdot}CH(OH){\cdot}CCl_3]_2;$$

it is indifferent towards concentrated sulphuric acid at 130°, but is resolved by alcoholic potash into oxalic and glycollic acids.

M. O. F.

Production of Diacetyl from Acetaldehyde. By Hans von Pechmann (*Ber.*, 1898, 31, 2123—2125. Compare Abstr., 1898, i, 62).—The author has already shown (*loc. cit.*) that one of the products obtained when phenylhydrazine acts on formaldehyde in acetic acid solution is glyoxalosazone. A similar reaction takes place when acetaldehyde is used, but in the case of the higher aldehydes no osazones are formed.

It is probable that the hydrazone of the aldehyde is the first product, and that this is then oxidised in the following way. $2CHMe{:}N{\cdot}NHPh - H_2 = NHPh{:}CMe{\cdot}CMe{:}NHPh$, since acetaldehydephenylhydrazone, when heated in acetic acid solution with phenylhydrazine, affords 10 per cent. of the theoretical amount of diacetylphenylhydrazone (compare Japp and Klingemann, Trans., 1888, 542). The oxidation may also be accomplished by means of mercuric oxide.

If a cold solution of acetaldehydephenylhydrazone in glacial acetic acid is treated with potassium permanganate, several products are obtained. One of these is volatile in steam, and crystallises from strong hydrochloric acid in shining leaflets melting at 71°; the mother liquor from the latter, when steam distilled, yields acetophenone and a nitrogenous substance which has not yet been characterised.

A. L.

Oxidised Cotton Oil. By WILHELM FAHRION (*Zeit. angw. Chem.*, 1898, 781—785).—See this vol., ii, 628.

Japanese Wood-oil. By JOHN H. B. JENKINS (*Analyst*, 1898, **23**, 113—116).—This is an oil of high density varying from 0·9343 to 0·9385. Its viscosity at 15·5° is also very considerable, varying from 858 to 1433 secs., water in the Redwood apparatus taking 28 secs.; its drying properties exceed those of linseed oil. In applying Maumené's heating test, it is necessary to largely dilute the sample with olive oil, as otherwise a solid mass will be obtained. Another peculiarity of this oil is that it produces a jelly with solution of iodine in chloroform or other solvents, but bromine does not cause it to solidify. Its iodine number, as determined by the Hübl method, varies from 149·7 to 165·7, but, unlike other oils, there is not the same remarkably constant ratio between the temperature rise, on treatment with bromine, and the iodine value (Abstr., 1895, ii, 427), and instead of the factor 5·7, the figure 7·0 should be used.

When the oil is heated out of contact with air for a few hours at 250°, it solidifies to a sticky, elastic mass on cooling. According to Cloëz, exposure to sunlight for a few days also causes the oil to solidify. The oil has no action on polarised light, but it has a very high refractive power = 1·503 at 19°.

Although resembling linseed oil in some respects, it is plain that it contains an acid which is not one of the ordinary unsaturated type.

L. DE K.

Change Produced in Oleic Acid on Keeping. BY MICHAEL VON SEŃKOWSKI (*Zeit. physiol. Chem.*, 1898, **25**, 434—439).—E. Salkowski has already pointed out that when oleic acid is kept for a length of time, it is partially converted into a solid substance melting at 48°. The author has submitted this substance to closer investigation, and after determining the acid value, ether value, saponification value, iodine value, and acetyl value, concludes that it is a mixture of 32·07 per cent. of oleic acid, 8·3 per cent. of stearolactone, 20·6 per cent. of hydroxystearic acid, and 39 per cent. of some unknown substance, possibly a hydroxystearic acid, as, on analysis, it gave numbers closely agreeing with those required for such a substance.

As an explanation of this change, it is suggested that oleic acid is first converted into a lactone, according to the following equation, $C_nH_{2n+1}\cdot CH\colon CH\cdot C_{n+2n}\cdot COOH = C_nH_{2n+1}\cdot CH_2\cdot CH\!<\!\begin{smallmatrix}C_nH_{2n}\\ -O-\end{smallmatrix}\!>\!CO$, and that the lactone then takes up water with formation of hydroxystearic acid.

A. W. C.

Tautomerism of Ethylic Acetoacetate. By KARL SCHAUM (*Ber.*, 1898, 31, 1964—1967).—The author maintains that the addition of a substance such as sodium ethoxide or pyridine to ethylic acetoacetate cannot, as stated by Schiff (this vol., i, 355), alter the state of equilibrium between the ketonic and the enolic forms of the compound, but can only alter the rate at which the equilibrium between these forms is attained. The addition of either of these substances in small amount is found to produce no alteration in the density or index of refraction of the compound, whereas the refraction of the two forms should differ considerably. That some change does take place when the freshly distilled compound is allowed to remain, is shown by the fact that the density gradually increases for some hours after distillation.

The author is unable to account for the transformation of the compounds of ethylic acetoacetate with benzylideneaniline by small amounts of sodium ethoxide or pyridine as described by Schiff.

A. H.

The Oxime of Ethylic Diethylacetoacetate. By MARIO BETTI (*Gazzetta*, 1898, 28, i, 274—276).—The oxime of ethylic diethylacetoacetate, $NOH\dot{:}CMe\cdot CEt_2\cdot COOEt$, obtained by heating the ethylic salt with hydroxylamine hydrochloride, sodium carbonate, and absolute alcohol on the water bath, forms in beautiful, colourless crystals melting at 56—57°, and is not a mobile liquid, as was stated by Westenberger (Abstr., 1884, 581). It forms a crystalline sodio-derivative with sodium ethoxide, and is precipitated unaltered from the solution by hydrochloric acid; the oxime is soluble in fuming hydrochloric acid or concentrated sulphuric acid, and is precipitated unchanged on adding water. The *benzoyl* derivative,

$$NOBz\dot{:}CMe\cdot CEt_2\cdot COOEt,$$

prepared with benzoic chloride and soda, crystallises in white needles melting at 70—71°. W. J. P.

ω-Dimethyllevulinic Acid or δ-Dimethyllevulinic (2-Methylhexan-3-onoic) Acid. By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1898, 31, 2311—2312).—ω-Dimethyllevulinic acid (Abstr., 1897, i, 247), produced by oxidising β-tanacetogendicarboxylic acid, is identical with δ-dimethyllevulinic acid prepared by Fittig and Silberstein (Abstr., 1895, i, 207; compare also Fittig and Wolff, Abstr., 1896, i, 136). The *oxime* separates from hot benzene in lustrous crystals, and melts at 88—89°; it yields a *silver* salt, which dissolves sparingly in boiling water. M. O. F.

Derivatives of Ethylmalonic Acid. By L. T. C. SCHEY (*Rec. Trav. Chim.*, 1897, 16, 356—360).—The ethylic salts of malonic, ethylmalonic, and diethylmalonic acids were separated by Romburgh's method (*Rec. Trav. Chim.*, 1887, 5, 235).

Ethylmalonomethylamide, $CHEt(CO\cdot NHMe)_2$, was obtained by adding ethylic ethylmalonate to twice the requisite quantity of methylamine hydrochloride, and pouring this mixture into 5N potassium hydroxide, the mixture being kept for three days in a well-stoppered flask, which was shaken at intervals. The excess of the amine was then neutralised with hydrochloric acid, and the dimethyl-

amide crystallised first from benzene and then from chloroform. The yield was about 80 per cent. of the theoretical. The amide is sparingly soluble in ether or light petroleum, easily in alcohol, water, chloroform, or benzene, but does not readily crystallise from these solvents. Its melting point is 177°.

The *dimethylamide*, $CHEt(CO\cdot NMe_2)_2$, was obtained by passing a current of dimethylamine through an ethereal solution of ethylmalonic chloride. On evaporating the ether, tetramethylamide is obtained in crystals melting at 76·5°; it is only sparingly soluble in light petroleum, but dissolves readily in other solvents. J. J. S.

Formation of Anhydrides of Aliphatic Dicarboxylic Acids. By KARL AUWERS (*Ber.*, 31, 1898, 2112—2113).—Blanc (*Bull. Soc. Chim.*, 1898, [ii], 19, 285) has laid much stress on the observation of Oddo and Manuelli (Abstr., 1897, i, 180) that camphoric acid, like succinic acid and unlike glutaric acid, readily yields its anhydride when treated in dilute alkaline solution with acetic anhydride. The author finds, however, that no importance can be attached to this fact, as $\alpha\alpha\alpha_1$-trimethylglutaric acid and maleinoid $\alpha\alpha_1$-dimethylglutaric acid at once afford anhydrides when subjected to this treatment. The fumaroid form of $\alpha\alpha_1$-dimethylglutaric acid, however, is not altered when treated in this way, and in this respect resembles isocamphoric acid.

Investigation of succinic acid and its methyl-substitution derivatives has shown that an increase in the number of methyl groups in the molecule facilitates the formation of anhydride. A. L.

α-Ethylideneglutaric Acid. By FRITZ FICHTER and AUGUST EGGERT (*Ber.*, 1898, 31, 1998—2001; Abstr., 1897, i, 13).—α-Ethylideneglutaric acid is the name given to the acid produced by intramolecular change during the distillation of δ-caprolactone-γ-carboxylic acid, and the authors adduce further evidence in support of the constitution, $CHMe{:}C(COOH)\cdot CH_2\cdot CH_2\cdot COOH$. The *silver, barium,* and *acid* and *normal calcium* salts have been prepared. The acid can also be obtained by treating the ethylic salt of the above lactonic acid with sodium ethoxide, and subsequently hydrolysing the sodium ethylic α-ethylideneglutarate thus produced. These reactions show that α-ethylideneglutaric acid stands in the same relation to δ-caprolactone-γ-carboxylic acid that the substituted itaconic acids do to the corresponding paraconic acids. When α-ethylideneglutaric acid is distilled, or treated with acetic chloride, an *anhydride* is produced which crystallises from ether and petroleum in needles melting at 87°; sodium amalgam reduces the acid to α-ethylglutaric acid (Abstr., 1896, i, 642).

The hydrogen bromide additive compound, which crystallises from petroleum in hemispherical aggregates melting at 88—89°, must have the constitution $CHMeBr\cdot CH(COOH)\cdot CH_2\cdot CH_2\cdot COOH$, since on boiling with water it yields γδ-hexenoic acid, hydrogen bromide, and carbonic anhydride, and this reaction is characteristic of the hydrobromide compounds of αβ-unsaturated acids containing bromine in the β-position.

γδ-Dibromethylglutaric acid, formed on adding bromine to α-ethylideneglutaric acid, crystallises from chloroform in lustrous needles,

and melts at 157—160°; when boiled with water, it decomposes into γ-bromo-γδ-hexenoic acid, hydrogen bromide, and carbonic anhydride. α-Ethylideneglutaric acid, when boiled with caustic soda, is converted into an isomeride, which crystallises from benzene or chloroform in small needles, melting at 97—98°. It yields the same hydrogen bromide additive compound as the original acid, but forms a different dibromide; accordingly, the authors suppose the new acid to be α-vinylglutaric acid, $CH_2{:}CH\cdot CH(COOH)\cdot CH_2\cdot CH_2\cdot COOH$, produced by a shifting of the double linking from the αβ- to the βγ-position.

G. T. M.

Synthesis of Symmetrical β-Hydroxytetramethylglutaric Acid. By EDMOND E. BLAISE (*Compt. rend.*, 1898, **126**, 1808—1810).—Reformatsky has shown that ethylic formate interacts with two molecules of ethylic α-bromopropionate in presence of metallic zinc to form αα-dimethyl-β-hydroxyglutaric acid, and, in accordance with this reaction, it was expected that the action of ethylic formate on a mixture of ethylic bromisobutyrate and bromacetate would give rise to unsymmetrical β-hydroxydimethylglutaric acid. In reality, however, the ethylic formate interacts with two molecules of the ethylic bromisobutyrate to form *symmetrical ethylic β-hydroxytetramethylglutarate*, and also with the ethylic bromacetate to form ethylic propan-1-al-3-oate, $CHO\cdot CH_2\cdot COOEt$, which immediately condenses to ethylic trimesate, with elimination of $3H_2O$. At the same time, the ethylic formate reacts with 1 mol. of ethylic bromisobutyrate to form small quantities of a substance of aldehydic nature, probably of the formula $CHO\cdot CMe_2\cdot COOEt$; this could not be isolated.

Symmetrical ethylic β-hydroxytetramethylglutarate yields, on hydrolysis, the corresponding *acid*, which crystallises with difficulty from a mixture of benzene and ethylic acetate, and melts at 169—170°. When treated with acetic chloride, it yields the *anhydride* of the corresponding acetyl derivative, which crystallises in prisms melting at 90°. This anhydride is converted by the action of aniline into a *phenylamide*, crystallising in needles melting at 157°; it loses water on heating, and forms a *phenylimide*, which melts at 178°. Acetoxytetramethylglutaric anhydride, when boiled with water, yields an *acid* which readily crystallises in prisms melting at 171°. When β-hydroxytetramethylglutaric acid is heated at 135° with hydriodic acid, it is reduced to *symmetrical tetramethylglutaric acid* which melts at 113°.

N. L.

Acidic Character of Unsaturated Organic Radicles. By FERDINAND HENRICH (*Ber.*, 1898, **31**, 2103—2105).—The reactivity of the methylene group in ethylic acetoacetate is attributed to its attachment to two acidic radicles. In diethylic glutaconate, the methylene group, although attached to only one acidic radicle, namely, carbonyl, is also joined to an unsaturated residue, $CH{:}CH$, and it still possesses the power of acting very readily, so that with methylic iodide and sodium ethoxide both mono- and dimethylglutaconic acids are obtained. The unsaturated radicle appears, therefore, to play the same part as the acidic carbonyl group.

Resorcinol is known to yield derivatives corresponding with its ketonic form (Abstr., 1887, 809, and 1888, 263), and this form resembles diethylic glutaconate in containing the grouping

$$OC\cdot CH{:}CH\cdot CH_2\cdot CO;$$

it also contains another methylene group attached to the two carbonyl groups. If the author's view be correct, resorcinol should be capable of yielding tetralkyl derivatives. Herzig and Zeisel (Abstr., 1890, 1404) obtained a tetrethylresorcinol to which they gave the constitution $\begin{matrix} HC\cdot CO—CEt_2 \\ HC\cdot CEt{:}C\cdot OEt \end{matrix}$, since it lost one ethyl group on treatment with hydriodic acid. The formation of such a substance is most readily explained if it is supposed that the triethyl derivative which is first produced changes from the form $\begin{matrix} HC\cdot CO—CEt_2 \\ HC\cdot CHEt\cdot CO \end{matrix}$ to the form $\begin{matrix} HC\cdot CO\cdot CEt_2 \\ HC\cdot CH{:}C\cdot OEt \end{matrix}$, which, on further ethylation, yields the tetrethyl compound.

These results lead to the expectation that a methylene group attached to an unsaturated radicle and also to a carbonyl group will generally react like a methylene group attached to two of these acid groups. Resorcinol in its ketonic form contains two such methylene groups, and when acted on by nitrous acid forms di-isonitrosoresorcinol, just as ethylic acetoacetate yields an isonitroso-compound when similarly treated. Phenol yields quinonemonoxime with nitrous acid, probably because its ketonic form, $\begin{matrix} CH\cdot CO—CH \\ CH\cdot CH_2\cdot CH \end{matrix}$, contains a methylene group attached to two unsaturated radicles. G. T. M.

Derivatives of Glutaconic Acid. By GEORGIO ERRERA (*Gazzetta*, 1898, **28**, i, 268—274).—Claisen's ethylic ethoxymethylenemalonate (Abstr., 1897, i, 592) reacts readily with ethylic sodiocyanacetate in absolute alcoholic solution, yielding the substance which the author previously considered to be diethylic $\alpha\gamma$-cyanocarboxyglutaconate (this vol., i, 297); it is, however, the ethylic dihydroxynicotinate,

$$CH{<}\begin{matrix} C(COOEt)\cdot C(OH) \\ C(COOEt){:}C(OH) \end{matrix}{>}N,$$

described by Guthzeit (Abstr., 1894, i, 71). When heated rapidly, it melts at 199°. W. J. P.

Racemic Decomposition of Rubidium Racemate. By JACOBUS H. VAN'T HOFF and WOLF MÜLLER (*Ber.*, 1898, **31**, 2206—2212).—The authors have investigated Traube's rubidium racemate crystallising with $2H_2O$, and have compared it with Wyrouboff's anhydrous form of the twinned tartrates.

According to Traube, the decomposition of the crystallised racemate into the anhydrous tartrates should be accompanied by a partial fusion; small experiments have shown that this occurs at temperatures between 40° and 50°. Experiments with the dilatometer gave no decisive results, as the change in volume on conversion is so small; further experiments were made by the aid of a thermometer. This is the first time racemic decomposition has been studied in this way,

and the maximum of four experiments gave 40—41° (corr.). 23·5 grams of the salt was heated with a little water, and the solution stirred with a Beckmann thermometer divided in 1/100ths of a degree. The air jacket around the vessel was in a thermostat provided with an Ostwald's calcium chloride regulator, by which means the temperature was kept at about 39°, and did not vary 0·1 degree. A racemic crystal was added, and the rise in temperature observed; a fresh crystal was then added, and the maximum temperature again read, and the operation repeated until a constant maximum was obtained. That the conversion was really a racemic one, that is, was a conversion into *d*- and *l*-tartrates, was proved by adding an excess of *d*-tartrate, this was found to have no effect on the temperature of conversion. (Compare Löwenherz, Abstr., 1896, ii, 149; van't Hoff and Dawson, this vol., i, 299). The authors have determined the solubilities—(1) of the racemate; (2) of the mixed tartrates; (3) of a mixture of racemate and *d*-tartrate, and (4) of the single tartrates. The solubilities were determined by the aid of a Kenrick's apparatus, and the determination of the tartrate in presence of the racemate was made polarimetrically by Kenrick's method (Abstr., 1897, i, 506), ammonium molybdate being added in order to increase the rotation.

The results are given in the form of curves, and also of a space model. J. J. S.

Malonic Methylanilide. By DANIEL VORLÄNDER and PAUL HERRMANN (*Ber.*, 1898, 31, 1826—1828).—Malonic methylanilide $CH_2(CO{\cdot}NMePh)_2$, was prepared by heating malonamide with methyl aniline, first at 200°, and finally to 240°, distilling over the unchanged methylaniline with steam, and purifying the residue either by crystallisation from an ethereal solution, or by fractional precipitation of this solution with light petroleum. When it is dissolved in benzene and treated with sodium, hydrogen is evolved, and when a benzene solution of iodine is added to this, the liquid filtered from sodium iodide yields *ethanetetracarboxylic methylanilide*, $C_2H_2(CO{\cdot}NMePh)_4$; this melts at 231°, and yields succinic acid when it is boiled with hydrochloric acid. At the same time, in company with the precipitated sodium iodide, there is formed a small quantity of a substance that melts and decomposes at 164°, and is apparently *iodomalonic methylanilide*, $CHI(CO{\cdot}NMePh)_2$; this substance is even the main product when the iodine, in absolute alcoholic solution, is added rapidly.

When an absolute alcoholic solution of sodiomalonic methylanilide is heated for 6 hours on a water bath with ethylic cinnamate, and the whole then allowed to remain for 20 days with excess of aqueous potash, methylaniline is formed, and dilute sulphuric acid precipitates an oil from which, after hydrolysing it with hydrochloric acid, cinnamic and β-phenylglutaric acids can be isolated (the *methylic* salt of the latter melts at 86—87°). Malonic methylanilide must thus have added itself on to ethylic cinnamate in the same way as ethylic malonate does. C. F. B.

Methylasparagine. By ARNALDO PIUTTI (*Ber.*, 1898, 31, 2039—2053).—The author has previously shown that at 105—110°,

alcoholic ammonia reacts with maleic anhydride, yielding β-asparagine (Abstr., 1897, i, 669).—Alcoholic ammonia also reacts with citraconic anhydride at 108—110°, the product being a racemic form of two enantiomorphic methylasparagines. The reaction is best carried out in a bronze autoclave; 30 c.c. of the anhydride is first introduced and then 250 c.c. of saturated alcoholic ammonia is carefully run in so that the two liquids form separate layers, a crystalline deposit being formed where the two liquids meet. After the autoclave is closed, the liquids are well mixed and then heated for 6 hours at 108—110° with constant shaking. When cold, the alcoholic liquid is removed from the solid deposit and the alcohol distilled; the residue from this is mixed with the solid deposit, dissolved in water, and converted into the *copper* derivative, $(C_5H_9N_2O_3)_2Cu + 2H_2O$, which crystallises in hexagonal lamellæ [$a : b : c = 1·96951 : 1 : ?$; $\beta = 88° 06'$] of a brilliant blue colour. The methylasparagine itself is best obtained by precipitating the copper, by the aid of hydrogen sulphide, in the presence of lead carbonate; by this means, the formation of colloidal copper sulphide is avoided. Methylasparagine (glutamine), $C_5H_{10}N_2O_3 + H_2O$, crystallises from concentrated solutions in glassy, rhombic plates [$a : b : c = 1·7141 : 1 : 1·43763$], loses its water of crystallisation when exposed to the air, and when sealed in a glass tube and left for several months, gradually deliquesces. It crystallises from alcohol in an anhydrous form, turns yellow at about 240°, and melts and decomposes at 254—256°. Its solutions are optically inactive and are not precipitated by silver nitrate, by barium chloride, or by calcium chloride. Like asparagine, it combines with acids to form salts which are very readily soluble.

Methylaspartic acid (glutamic acid), $C_5H_9NO_4$, is obtained when anhydrous methylasparagine (15 grams) is boiled for 2 hours with hydrochloric acid (56·8 c.c. containing 7·821 grams of hydrogen chloride) and then treated with the requisite quantity of aqueous ammonia (28·4 c.c.). The precipitated acid thus obtained can best be purified by repeated crystallisation from boiling water; it forms crusts of small, prismatic needles, which melt and decompose at 232—234°. The crystals contain $1H_2O$, which they only lose completely when heated to 180°. The acid is insoluble in ether, and almost insoluble in absolute alcohol, but dissolves in hot dilute alcohol; it has a sweet, acid taste and is optically inactive; it forms salts with both bases and acids, the *copper* salt, $C_5H_7CuNO_4 + 4H_2O$, obtained by treating an aqueous solution of the acid with the requisite amount of copper acetate, crystallises in blue, hexagonal prisms, which are very sparingly soluble in water. When a concentrated aqueous solution of the acid is treated with nitrous acid, an acid identical with Carius's α-methylmalic acid is obtained. The author has prepared this acid by a method slightly different from that employed by Carius (*Annalen*, 1864, **129**, 160) in order to compare it with his own.

Since α-methylmalic acid is the racemic form of the two enantiomorphs, $COOH·CH_2·CMe(OH)·COOH$, it follows that the methylaspartic acid must be the racemic form of α-methylaspartic acid,

$$COOH·CH_2·CMe(NH_2)·COOH,$$

and methylasparagine must be the racemic form of either $CONH_2 \cdot CH_2 \cdot CMe(NH_2) \cdot COOH$ or $COOH \cdot CH_2 \cdot CMe(NH_2) \cdot CONH_2$.

J. J. S.

"Oxymercarbides." By KARL A. HOFMANN (*Ber.*, 1898, **31**, 1904—1909).—When sodium (10 grams) is dissolved in alcohol (150 grams) and the solution boiled (16 hours) with finely-divided yellow mercuric oxide (40 grams), the residue contains, in addition to mercury and mercury oxide, a new substance, yellow in colour but turning grey when exposed to light, which appears to have the constitution $OHg_2{:}C(Hg \cdot OH) \cdot C(Hg \cdot OH){:}OHg_2$, and is a member of a class of compounds termed by the author *oxymercarbides.* When boiled with an aqueous solution of hydrazine, it yields nitrogen mixed with some ethane. It explodes violently at about 230°, but is not very sensitive to percussion. It is a diacid base, forming insoluble salts from which it is regenerated by treatment with alkalis; the *nitrate sulphate*, and *chloride* appear to have the constitution $C_2(Hg \cdot NO_3)_2(Hg \cdot OH)_4$, $C_2(Hg \cdot SO_4H)_2(Hg \cdot OH)_4$, and $C_2(HgCl)_6$ respectively. So firmly are the carbon and mercury united, that potassium cyanide does not separate them, but forms instead a yellow compound, $C_2Hg_2(HgCN)_2$.

Paraldehyde yields the same mercarbide, and acetone and propylic alcohol form analogous ones. Methylic alcohol, however, does not form a mercarbide.

C. F. B.

Action of Mercuric Nitrate on Acetaldehyde and on Ethylic Acetoacetate. By KARL A. HOFMANN (*Ber.*, 1898, **31**, 2212—2218).—Acetylene, when passed through a solution of mercuric nitrate acidified with nitric acid, yields a fine, colourless, crystalline precipitate, which, after washing with 2 per cent. nitric acid and drying under reduced pressure, has the composition $C_2Hg_2NO_4H$. (If the gas is passed through the solution for several hours, a black substance is also formed.) It is practically insoluble in water, or dilute (3 per cent.) nitric acid, but is decomposed by concentrated acid. With warm dilute hydrochloric acid, it yields acetaldehyde, and mercuric chloride goes into solution. When treated with alkalis, the nitrogen is obtained in the form of nitrates, and when warmed with sodium hydroxide and potassium cyanide solution, aldehyde resin is formed. The compound may be obtained in the form of large crystals by using an alcoholic solution of aldehyde in place of acetylene; after remaining for 14 days, large, colourless, doubly-refractive prisms, terminated by pyramids, are deposited. The constitution suggested is $NO_3 \cdot Hg \cdot C({:}Hg) \cdot CH{:}O$. The author suggests that the substance obtained by Poleck and Thümmel (Abstr., 1890, 118) by shaking commercial ether with an aqueous solution of mercuric chloride and potassium hydrogen carbonate, is probably a somewhat similar compound, only contaminated by a little mercurous chloride. A compound, $C_6H_8HgO_3$, may be obtained by adding ethylic acetoacetate to an acidified solution of mercuric nitrate, provided the nitrate solution is sufficiently dilute and that the temperature is kept below $+5°$; it is insoluble in water, and is decomposed when warmed with dilute nitric acid, the ethereal salt being regenerated. Acetone yields a pale yellow compound, $C_3Hg_3H_5O(NO_3)_2$. It thus

appears probable that mercury is able to replace hydrogen atoms attached to a carbon atom in the α-position relatively to an aldehydic or ketonic group.

The compound $C_2Hg_2NO_4H$, when heated with an ethereal solution of ethylic iodide (two molecules for each atom of mercury), yields a yellow substance, $C_2Hg_3I_2$, which is insoluble in water, dilute nitric acid, or potassium iodide solution. On exposure to light, it rapidly turns grey. Dilute aqueous sodium hydroxide decomposes the nitrate, $C_2Hg_2NO_4H$, yielding a black residue consisting largely of metallic mercury. If this residue is extracted with 5 per cent. sodium hydroxide, then with cold dilute nitric acid, and finally with 10 per cent. hydrochloric acid, a colourless residue of the compound, $C_2Hg_6Cl_6$, is obtained (preceding abstract). The filtrate from the black residue, when neutralised with carbonic anhydride, nitric acid, or the requisite quantity of hydrochloric acid, yields in each case a white precipitate. The *nitrate*, $C_2Hg_3NO_6H$, obtained when nitric acid is employed, yields no aldehyde when treated with hydrochloric acid or with alkali and potassium cyanide. The *chloride* has the composition $C_2Hg_3Cl_3O_2H$. These salts, when treated with alkali, leave a grey residue consisting of mercury and the explosive oxymercarbide, $C_2Hg_6O_4H_2$.

J. J. S.

Occurrence of Ketopentamethylene in Wood-oil. By HERMANN METZNER and DANIEL VORLÄNDER (*Ber.*, 1898, **31**, 1885—1886).—Ketopentamethylene can be detected in the products of the dry distillation of calcium succinate; by treating the fraction boiling at 100—160° with benzaldehyde and caustic soda, dibenzylideneketopentamethylene can be isolated. Furan appears also to be contained in the product.

Ketopentamethylene is probably always formed when wood is distilled, and if it has been found in but few examples of wood-oil, this is possibly because most manufacturers pass the crude products, while still in the gaseous state, through milk of lime, which may convert the ketopentamethylene into substances of high boiling point.

C. F. B.

Stereoisomeric 1:3-Pentamethylenedicarboxylic Acids. By KARL THEODOR POSPISCHILL (*Ber.*, 1898, **31**, 1950—1957).—*Cyclopentane*-1 : 1 : 3 : 3-*tetracarboxylic acid*, $\begin{matrix} CH_2\cdot C(COOH)_2 \\ | \\ CH_2\cdot C(COOH)_2 \end{matrix}\!\!>CH_2$, prepared by heating ethylic butanetetracarboxylate with sodium ethoxide and methylenic iodide, and hydrolysing the ethereal salt produced, forms a white, hygroscopic, crystalline mass which melts at 186—188°, vigorously evolving carbonic anhydride; the product of this change is cyclopentane-1 : 3-*cis-cis*-dicarboxylic acid, which is also formed on evaporating the aqueous solution of the tetracarboxylic acid.

The *anhydride* of cyclopentane-1 : 3-*cis-cis*-dicarboxylic acid, $C_7H_8O_3$, obtained by heating the crude acid with acetic anhydride in a reflux apparatus, crystallises from ethylic acetate in lustrous, monoclinic plates, melts at 160—161·5°, and boils at 215—218° under a pressure of 90 mm. The *acid*, $C_7H_{10}O_4$, crystallises from water in lustrous, flattened prisms, and melts at 120—121·5°.

Cyclopentane-cis-trans-*dicarboxylic acid*, $C_7H_{10}O_4$, produced on heating the foregoing acid at 180° during 4 hours, crystallises from carbon tetrachloride in small, flattened prisms, and melts at 87—88·5°; prolonged treatment with boiling acetic anhydride converts it into the anhydride of the *cis-cis*-modification. The *silver* salt is obtained from both acids as an amorphous precipitate, which is extremely sensitive to light and heat, and is almost insoluble in water. The *calcium* salt of the *cis-cis*-acid crystallises in monoclinic plates, and requires five times its weight of water to dissolve it at 30°; the *calcium* salt of the *cis-trans*-modification crystallises in nodules, and dissolves in its own weight of water; both salts contain $2\frac{1}{2}H_2O$. The *barium* salts are very readily soluble, and crystallise in slender needles; the *lead* salts are amorphous.

The *methylic* salt of the *cis-cis*-acid boils at 138—138·5° under a pressure of 25 mm. The *diamide* crystallises from water in slender needles and melts at 224—226°, yielding the *di-imide*, which melts at 154—155° and boils above 360°; the *dianilide* crystallises from methylic alcohol in leaflets, and melts at 222—224°. M. O. F.

Cyclic Compounds. By WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1898, **301**, 154—202).—This paper scarcely lends itself to condensation. After pointing out the advantages offered by Caucasian naphtha as a source of cyclic compounds, the author proceeds to the isolation of its constituents. Fractionations of some specimens of "benzin" are detailed, and the specific gravity of every fraction is recorded; from these data, curves are plotted, correlating density and boiling point. Great importance is attached to specific gravity, which is regarded as the best criterion of the state of purity in which the hydrocarbons are isolated from the mixture.

The belief that hexanaphthene yields dinitrobenzene under the influence of nitric acid is now found to be untenable. It is extremely difficult to separate benzene from cyclic hydrocarbons boiling at a much lower temperature than that substance, and, before this was realised, it was not unnatural to suppose that the dinitrobenzene obtained from the fraction boiling at 60—70° was produced at the expense of the hexanaphthene in the mixture, the more especially as the boiling point of the latter underwent no change in the process; if, however, triphenylmethane is dissolved in the hydrocarbons, and the solution cooled, the benzene compound of triphenylmethane crystallises from the mixture, which then yields dinitrobenzene no longer.

Directions are given for preparing the chlorides, bromides, and iodides of the naphthenes, and also their nitro-, amido-, and hydroxy-derivatives; the conversion of the naphthenes into naphthylenes, and the behaviour of the former towards oxidising agents, are described, and it is pointed out that, under favourable conditions, cyclic hydrocarbons which do not contain a side chain are converted by nitric acid into dibasic acids containing the same number of carbon-atoms.

M. O. F.

Derivatives of Cycloheptane. By EDUARD BUCHNER and ANDREAS JACOBI (*Ber.*, 1898, **31**, 2004—2009. Compare this vol., i, 301).—The authors call attention to the great similarity existing between

their seven-membered ring compounds derived from suberone and the so-called ethylcyclopentane derivatives, obtained by Einhorn and Willstätter from paramethylenedihydrobenzoic acid (Abstr., 1894, i, 524), and they suggest that the two series may, in reality, be identical; this view is supported by the fact that derivatives of both series are convertible into paratoluic acid.

Chlorosuberanecarboxylic acid (1-*chlorocycloheptanecarboxylic acid*), $C_7H_{12}Cl\cdot COOH$, obtained either by heating hydroxysuberanecarboxylic acid with hydrochloric acid, or by warming it with phosphorus pentachloride on the water bath, crystallises from weak alcohol in colourless leaflets melting at 42—44°. This acid forms the starting-point in the preparation of the suberenecarboxylic acid and its amide, and of suberanecarboxylic acid and its amide; these compounds which were only briefly alluded to in a previous communication (this vol., i, 301), are now more fully described.

Suberenecarboxylic acid dibromide (1:2-*dibromocycloheptanecarboxylic acid*), $C_7H_{11}Br_2\cdot COOH$, produced by adding bromine to suberenecarboxylic acid, forms a colourless, crystalline mass which melts at 135°.

Bromosuberanecarboxylic acid (1-*bromocycloheptanecarboxylic acid*), $C_7H_{12}Br\cdot COOH$, prepared by treating suberanecarboxylic acid with bromine and phosphorus, crystallises from hot formic acid in colourless needles melting at 89—91°. G. T. M.

Azelaone and Azelaol. By K. G. Hans Derlon (*Ber.*, 1898, **31**, 1957—1964).—When azelaic acid or its calcium salt is distilled with lime, a small amount of *azelaone*, $C_8H_{14}O$, is formed, which distils at 80—91° under a pressure of 22 mm. The compound with sodium hydrogen sulphite cannot be obtained pure, and the *oxime* has only been isolated in the form of an oil boiling at 140—160° under a pressure of 100 mm. The *semicarbazone*, $C_8H_{14}:N\cdot NH\cdot CO\cdot NH_2$, crystallises in colourless, lustrous prisms melting at 85°. On oxidation with potassium permanganate, this ketone yields a small amount of suberic acid, $C_8H_{14}O_4$, and this reaction proves that azelaone is the normal cyclo-octanone, $CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\CH_2\cdot CH_2\cdot CH_2\end{matrix}>CO$. On reduction with alcohol and sodium, it is converted into the corresponding alcohol, *azelaol*, $C_{18}H_{15}\cdot OH$, which is a colourless oil boiling at 187—188° under a pressure of 749 mm. A. H.

Dialdehyde of Adipic Acid. By Adolf von Baeyer and Hans von Liebig (*Ber.*, 1898, **31**, 2106—2110. Compare Abstr., 1897, i, 588).—When dihydroxysebacic acid is treated with lead peroxide, the dialdehyde of suberic acid is produced; dihydroxysuberic acid, under similar conditions, yields, not the dialdehyde of adipic acid, but a condensation product of this substance.

Dihydroxysuberic acid is best prepared by heating dibromosuberic acid with barium hydroxide; the employment of caustic potash results in the formation of amorphous products.

Δ^1-*Cyclopentenealdehyde* is the final product of the action of lead peroxide on dihydroxysuberic acid in the presence of acetic and phosphoric acids; it is separated from the mixture by distillation with steam, and when subsequently rectified, forms a colourless liquid with

a pungent odour resembling that of benzaldehyde. The yield obtained is very small and the substance readily decomposes; on this account, its boiling point was not determined. It is readily soluble in water, and on adding semicarbazide hydrochloride to the solution, the *semicarbazone* is obtained, crystallising from water or alcohol in hexagonal leaflets, and melting at 208°. The oxime does not crystallise, and the hydrazone forms colourless leaflets which speedily resinify.

Δ^1-Cyclopentenecarboxylic acid (Abstr., 1893, i, 557), resulting from the oxidation of the aldehyde with silver oxide, crystallises from water in leaflets or needles and melts at 120°. The copper salt forms blue, tabular crystals which change, on heating, into a white powder; the silver salt crystallises from water in hexagonal leaflets.

α-Hydroxyvaleric acid is readily converted into isobutaldehyde on treatment with lead peroxide and phosphoric acid; the semicarbazone of this aldehyde melts at 124°. G. T. M.

Pseudophenylacetic Acid. By EDUARD BUCHNER (*Ber.*, 1898, 31, 2241—2247).—The ethereal salt of this acid, which results from the action of ethylic diazo-acetate on benzene, is readily converted into two isomeric acids, the so-called α- and β-isophenylacetic acids (compare this vol., i, 314).

These two acids are both cycloheptatrienecarboxylic acids; they give rise to the same dihydrobromide and to a cycloheptanecarboxylic acid identical with that previously described under the name of suberanecarboxylic acid (Trans., 1881, 541); furthermore, they are closely related to the so-called paramethylenedihydrobenzoic acids obtained from the coca alkaloids, and are also derivatives of cycloheptatriene. Four cycloheptatrienecarboxylic acids are theoretically possible, and four such acids have been obtained. The isomerism depends on the positions occupied by the three double linkings in the heptatriene ring, and until these have been determined with certainty in the case of each isomeride, the acids will be distinguished as α-, β-, γ- and δ-cycloheptatrienecarboxylic acids.

	Former designation.	Reference.	M.p. of acid.	M.p. of amide.
α-Acid	α-Isophenylacetic acid.	Abstr., 1897, i, 282.	71°	129°
β-Acid	*p*-Methylenedihydrobenzoic acid. β-Isophenylacetic acid.	Abstr., 1893, i, 538. This vol., i, 314.	55° 55	101° 98
γ-Acid	*p*-Methylenedihydrobenzoic acid. γ-Isophenylacetic acid.	Abstr., 1895, i, 92. Succeeding abstract.	An oil ,,	90° 94—96
δ-Acid	*p*-Methylenedihydrobenzoic acid.	Abstr., 1893, i, 378	32°	125·5°

The author's previous suggestion that pseudophenylacetic acid has

the constitution, $COOH\cdot CH\!<\!\begin{matrix}CH\cdot CH\!:\!CH\\ CH\cdot CH\!:\!CH\end{matrix}$, is in accordance with subsequent investigations; its amide, on hydrolysis with caustic soda, readily yields α-isophenylacetic acid, which is probably $\Delta^{1\cdot 3\cdot 5}$-Cycloheptatrienecarboxylic acid; the reaction is assumed to take place in the following manner:—

$$COOH\cdot CH\!<\!\begin{matrix}CH\cdot CH\!:\!CH\\ CH\cdot CH\!:\!CH\end{matrix} \rightarrow COOH\cdot CH\!<\!\begin{matrix}CH(OH)\cdot CH\!:\!CH\\ CH_2 - CH{=}CH\end{matrix} \rightarrow$$

$$COOH - C\!\lessdot\!\begin{matrix}CH\cdot CH\!:\!CH\\ CH_2\cdot CH\!:\!CH\end{matrix}.$$

When isophenylacetic acid dihydrobromide, obtained from either α- or β-isophenylacetic acid, is reduced with sodium and amylic alcohol, cycloheptanecarboxylic acid and a crystalline compound, $C_8H_{12}O_3$, are obtained; the latter is acidic, melts at 125—126°, crystallises from ether in colourless prisms, and probably has the constitution $C_7H_{11}O\cdot COOH$. Its composition was previously given as $C_6H_{10}O_2$ (Abstr., 1897, i, 283).

The above dihydrobromide, when reduced with zinc dust and alcoholic hydrogen chloride, yields *bromocycloheptenecarboxylic acid* which melts at 150—151°; its amide, $C_7H_{10}Br\cdot CONH_2$, crystallises from ether in colourless needles and melts at 134—135°.

When heated with a solution of hydrogen bromide in acetic acid, isophenylacetic acid is converted into dibromotetrahydroparatoluic acid and *tribromocycloheptanecarboxylic acid*; the latter crystallises from ether in colourless rhombohedra, melts at 199°, and is not attacked by alkaline permanganate solution. The former product is identified by conversion into paratoluic and terephthalic acids. G. T. M.

β-Isophenylacetic Acid (β-Cycloheptatrienecarboxylic Acid). By Eduard Buchner and Ferdinand Lingg (*Ber.*, 1898, **31**, 2247—2250. Compare preceding abstract.)—This acid, when dissolved in glacial acetic acid saturated with hydrogen bromide, forms dibromocycloheptenecarboxylic acid, $C_7H_9Br_2\cdot COOH$, identical with that obtained from its α-isomeride. Both isomerides, on treatment with bromine in glacial acetic acid, give the same *tetrabromocycloheptenecarboxylic acid*, which crystallises from this solvent in prisms melting at 192—194°; the mother liquors from the experiment with the α-isomeride also yield a tetrabromide which melts at 176—178°, and is very probably identical with that melting at 174—175° obtained by Einhorn and Willstätter from paramethylenedihydrobenzoic acid (Abstr., 1894, i, 524). γ-Cycloheptatrienecarboxylic acid is produced on boiling the β-acid for 48 hours with alcoholic potash; it forms an oil which, on treatment with phosphorus pentachloride and ammonia, yields an amide melting at 94—97°. Einhorn and Willstätter (*loc. cit.*) obtained the same acid from the two crystalline paramethylenedihydrobenzoic acids.

G. T. M.

Chlorinating Action of Ferric Chloride in the Aromatic Series. By Victor Thomas (*Compt. rend.*, 1898, **126**, 1211—1214). —Ferric chloride readily chlorinates aromatic hydrocarbons, especially

on heating; hydrogen chloride is evolved, and there is much charring. The products obtained from benzene include chlorobenzene, 1 : 4-dichlorobenzene, 1 : 2 : 4-trichlorobenzene, 1 : 2 : 4 : 5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, and possibly small quantities of derivatives isomeric with these. Bromobenzene is converted by the action of ferric chloride into 1 : 4-chlorobromobenzene, whilst toluene yields a mixture of chlorotoluenes and derivatives richer in chlorine than these, substitution taking place only in the benzene nucleus. With benzylic chloride, there is produced a blackish resin, soluble in benzene, analogous to the substance $(CH_2Ph)_n$, which Friedel obtained by the interaction of benzylic chloride and aluminium chloride.

N. L.

Action of Bromine on Phenols in Presence of Aluminium Bromide. By F. Bodroux (*Compt. rend.*, 1898, **126**, 1282—1285).—The author has investigated the products obtained from phenols by the action of excess of bromine containing a small quantity of aluminium bromide. Phenol yields the pentabromophenol described by Körner; it forms long, silky needles which melt at 225°. Orthocresol, metacresol, and paracresol yield tetrabromo-derivatives which crystallise in long, white needles melting at 207—208°, 194°, and 198—199° respectively. Thymol yields tetrabromometacresol.

With polyhydric phenols, the reactions are less definite. Resorcinol yields a black, gummy mass; quinol yields some tetrabromoquinol mixed with more complex products.

Orthonitrophenol yields the 4 : 6 : 2-dibromonitrophenol melting at 117—118°, and paranitrophenol, the 2 : 6 : 4-dibromonitrophenol melting at 141°. In the case of these nitro-derivatives, the products are the same as in the absence of aluminium bromide.

C. H. B.

Action of Sulphuryl Chloride on Phenols and their Ethers. By Alberto Peratoner (*Gazzetta*, 1898, **28**, i, 197—240).—The author discusses at length the action of sulphuryl chloride on phenols and their ethers, and applies Nef's views as to the addition of halogen and subsequent elimination of hydrogen haloid to obtain an explanation of the reactions concerned.

[With G. B. Condorelli.]—Parachlorophenol alone is obtained by the action of pure sulphuryl chloride on phenol, but if the chloride be impure, 2 : 4-dichlorophenol is simultaneously formed.

5-*Chlororthocresol*, obtained by the action of sulphuryl chloride on orthocresol, crystallises in colourless needles melting at 48—49°, and its *benzoate*, $C_{14}H_{11}ClO_2$, forms colourless, pearly laminæ melting at 71—72°. The *methylic* ether has a pleasant odour, boils at 212·6—214·6° under 758·4 mm. pressure, and is oxidised by permanganate, yielding 5-*chloromethylsalicylic acid*, which crystallises in minute needles melting at 81—82°; its *barium* salt crystallises with $2H_2O$ in lustrous plates, and on warming the acid with hydriodic acid, it yields the 5-chlorosalicylic acid melting at 171—172·5°. *Orthotolylic benzoate* boils at 303—305°, and does not react with sulphuryl chloride.

6-*Chlorometacresol*, obtained by the action of sulphuryl chloride on metacresol, crystallises in long, colourless needles melting at 52—53°, and boils at 235·9° under a pressure of 757·7 mm.; its *methylic* ether

boils at 215·5—217·5° under 759 mm. pressure, and on treatment with alkaline permanganate yields 6-*chloro-3-methoxybenzoic acid*, $C_8H_7ClO_3$, which crystallises in colourless needles melting at 160—161°. When warmed with hydriodic acid, this acid gives 6-*chloro-3-hydroxybenzoic acid*, which melts at 169—170°; its constitution is determined by converting it into 4-chloro-2-nitrophenol.

Parachlorothymol, melting at 62—64°, is obtained by treating thymol with sulphuryl chloride; its constitution is evident from its yielding thymoquinone on oxidation with manganese dioxide and sulphuric acid. The *methylic* ether of parachlorothymol is a liquid boiling at 251° under 760·2 mm. pressure.

[With CARM. VITALI.]—Sulphuryl chloride reacts with parabromophenol at the ordinary temperature, giving a small quantity of parachlorophenol melting at 37° (compare Ling, Trans., 1892, **61**, 560). The *benzoate* of parabromophenol melts at 102—103°, and does not react with sulphuryl chloride. Mazzara and Lamberti (Abstr., 1897, i, 182) have already shown that 3-chloro-1 : 4-cresol is obtained on treating paracresol with sulphuryl chloride; the *methylic* derivative, C_8H_9OCl, boils at 215—218° under 760·8 mm. pressure, and yields 3-chloranisic acid melting at 212—214° on oxidation with alkaline permanganate. *Paratolylic benzoate* melts at 141°.

Isopropylphenol reacts with sulphuryl chloride, yielding 3-*chlorisopropyl*-4-*phenol*, a liquid which boils at 230—232° under 760 mm. pressure, and does not crystallise at $-18°$; its *methylic* derivative, $C_{10}H_{13}ClO$, is a colourless oil of aromatic odour boiling at 246·7—248·7° under 759·4 mm. pressure, and yields 3-chloranisic acid on oxidation with permanganate.

Paracumophenol acetate boils at 238—240°, and is but slightly acted on by sulphuryl chloride. Parabenzylphenol is, however, converted into a *chlorobenzylphenol*, $C_{13}H_{11}ClO$, which boils at 318—321°, with partial decomposition, in a current of carbonic anhydride; it is not volatile in a current of steam. *Parabenzylphenol acetate* boils at 310°, and is only slightly attacked by sulphuryl chloride. Paranitrophenol and its benzoate, and also picric acid are not acted on by sulphuryl chloride.

Catechol and sulphuryl chloride react violently, but by using ether as a solvent, and cooling, a *monochlorocatechol*, $C_6H_5ClO_2$ [OH : OH : Cl = 1 : 2 : 4], is obtained; it crystallises in lustrous scales melting at 80—81°, and its methylic derivative is identical with the monochloroveratrole described below. The use of a larger proportion of sulphuryl chloride leads to the formation of a *dichlorocatechol*, $C_6H_4Cl_2O_2$ [OH : OH : Cl_2 = 1 : 2 : 4 : 5], which crystallises in colourless needles melting at 105—106°, and is converted into 1 : 2 : 4 : 5-tetrachlorobenzene by phosphorus pentachloride; the dichlorocatechol, on methylation, gives the dichloroguaiacol melting at 71—72°. Catechol monobenzoate is not acted on by sulphuryl chloride.

Sulphuryl chloride reacts with pyrogallol, yielding a *monochloropyrogallol*, $C_6H_5ClO_3$, melting at 143°, of which the benzoate melts at 140°, and of a *dichloropyrogallol* melting at 128°, of which the *benzoate* melts at 165°; the trichloropyrogallol obtained by Webster (Trans., 1884, **45**, 205), and melting at 175°, is also formed.

[With G. ORTOLEVA.]—Parachloranisoil and parachlorophenetoil are respectively obtained by the action of sulphuryl chloride on anisoil and phenetoil. The methylic ethers of ortho- and para-cresol similarly yield the methylic ethers of parachlororthocresol and orthochloropara-cresol; these, on oxidation with permanganate, give 5-chloromethyl-salicylic acid melting at 81—82°, and 3-chloranisic acid melting at 213° respectively. Thymol methylic ether, on treatment with sulphuryl chloride, yields the methylic ether of parachlorothymol described above.

Monochloroguaiacol, $C_7H_7ClO_2$, is obtained as a colourless oil on treating guaiacol with sulphuryl chloride; it boils at 239—241·5° under 757·7 mm. pressure, and, on methylation, yields the monochloro-veratrole described below; the *benzoate*, $C_7H_6BzClO_2$, crystallises in tiny, colourless scales melting at 76—77°. Using a larger proportion of sulphuryl chloride, a dichloroguaiacol, $C_7H_6Cl_2O_2$, which crystallises in long, colourless needles melting at 71—72°, is obtained; its *benzoate*, $C_7H_5BzCl_2O_2$, melts at 72—74°. With a yet larger proportion of sulphuryl chloride, a *trichloroguaiacol*, $C_7H_5Cl_3O_2$, crystallising in colourless needles melting at 107—108° is obtained; its *benzoate*, $C_7H_4BzCl_3O_2$, melts at 128—129°. Guaiacol acetate is not acted on by sulphuryl chloride.

With sulphuryl chloride, veratrole yields *monochloroveratrole*,

$$C_8H_9ClO_2\ [OMe : OMe : Cl = 1 : 2 : 4],$$

as a colourless oil boiling at 242·4° under 763·3 mm. pressure, and also *dichlorovertarole*, $C_8H_8Cl_2O_2$ [$OMe : OMe : Cl_2 = 1 : 2 : 4 : 5$], which crystallises in colourless needles melting at 85·5—86·5°.

Ortho-, meta-, and para-hydroxybenzoic, protocatechuic, thymotic, paracumophenolorthocarboxylic, benzoic, and methylsalicylic acids, and the ethylic salts of the phenolsulphonic acids, are not acted on by sulphuryl chloride; but salicylaldehyde yields the 5-chlorosalicylaldehyde melting at 98°, and parahydroxybenzaldehyde gives the 3-chloro-derivative melting at 148°. Vanillin yields a *chloro*-derivative, $C_8H_7ClO_3$, with sulphuryl chloride; this crystallises in colourless, lustrous laminæ melting at 158—160°.

Ethylic phenylic carbonate, salol, and triphenylic phosphate do not react with sulphuryl chloride. Phenylic oxide yields a mixture of mono- and dichloro-derivatives which could not be separated, whilst xanthen gives a *dichloro*-derivative, $C_{13}H_8Cl_2O$, which melts at 148—149°, and apparently yields a dichloroxanthone melting at 181° on oxidation.

Phenyl benzyl ketone gives, with sulphuryl chloride, a *trichloro*-derivative boiling at 160—175°; this could not be purified, but, on heating with hydrochloric acid in a sealed tube, yields 2 : 4 : 6-trichlorophenol.

Phenoxyacetic acid is converted by sulphuryl chloride into parachlorophenylacetic acid, which crystallises in colourless needles melting at 150—151°, and, on hydrolysis with fuming hydrochloric acid, yields parachlorophenol. W. J. P.

Alkylanisoils and Alkylphenetoils. I. Orthethylphenetoil. By PAUL JANNASCH and WILLY HINRICHSEN (*Ber.*, 1898, 31, 1824).—Iodophenetoil (25 grams), prepared from phenetidine by Sandmeyer's

reaction, and ethylic iodide (20 grams) were diluted with benzene, heated with sodium (8 grams) for 4—5 hours at 120—140°, and then allowed to remain for some time. The whole was then filtered, the solid residue washed with benzene, and the united filtrates distilled, the part boiling above 125° being then fractionated carefully. *Orthethylphenetoil*, $C_6H_4Et\cdot OEt$, boils at 189—192°. C. F. B.

Derivatives of Ethylenecatechol [Catechol Ethylenic Ether]. By CHARLES MOUREU (*Compt. rend.*, 1898, **126**, 1426—1428).—Catechol ethylenic ether is readily obtained in quantity by heating catechol with potash, ethylenic bromide, and water, in a reflux apparatus filled with hydrogen to prevent oxidation. It is an oily liquid, insoluble in water, boiling at 216° (corr.), and having a sp. gr. = 1·186 at 0°. Potassium permanganate, hydriodic acid, and ammonia have no action on it, even at high temperatures, whilst chromic acid oxidises it completely to oxalic and carbonic acids. Substitution derivatives in which the ethylene group is concerned are best obtained indirectly. Thus, by the action of dibromhydrin, $CH_2Br\cdot CHBr\cdot CH_2\cdot OH$, on the sodium derivative of catechol, the *compound*, $C_6H_4<\begin{matrix}O\cdot CH_2\\ \vert\\ O\cdot CH\cdot CH_2\cdot OH\end{matrix}$, is obtained which crystallises in fine, colourless needles melting at 89—90° and boiling without decomposition at 283—286°. The corresponding *acetate* boils at 185—188° under a pressure of 30 mm. The sole product of the action of nitric acid on catechol ethylenic ether was found to be the mononitro-derivative, melting at 121°, which has previously been obtained by Vorländer, and appears, from the following considerations, to have the constitution $C_6H_3(NO_2)<\begin{matrix}O\cdot CH_2\\ \vert\\ O\cdot CH_2\end{matrix}$ [O : O : NO_2 = 1 : 2 : 4].

When the sodium derivative of protocatechuic aldehyde, the constitution of which is known to be [OH : OH : CHO = 1 : 2 : 4], is treated with ethylenic bromide, it is converted into *protocatechuic aldehyde ethylenic ether* or *homopiperonal*, which crystallises in long, silky needles melting at 50—51·5° and boiling at 299°. It forms a *phenylhydrazone* melting at 107—108° and an *oxime* melting at 75—75·5°. The latter, on dehydration, yields a *nitrile*, which crystallises in fine needles melting at 105°. On reduction with stannous chloride, the nitro-derivative obtained from catechol ethylenic ether yields, the corresponding *amido*-derivative, which is a heavy, thick liquid, insoluble in water, and boiling at 162° under a pressure of 9 mm. The *hydrochloride* of this base melts and decomposes at about 220°, the *picrate* at about 180°, and the *platinochloride* at 213°. The diazo-derivative, on treatment with cuprous cyanide, yields a nitrile which is identical with the product obtained from homopiperonaloxime (see above). The *acid* resulting from its hydrolysis melts at 137°.

It should be noted that the dimethylic ether of catechol forms a nitro-derivative analogous to that yielded by catechol ethylenic ether, the nitro-group taking up the para-position with regard to one of the alkyloxy-groups. This behaviour may be contrasted with that of substances containing, like naphthalene, two aromatic nuclei, in which case the substituting nitro-group takes up the meta-position. N. L.

Oxidation of Pyrogallol in Presence of Alkalis. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, **126**, 1459—1467).—In presence of 3 molecules of potassium hydroxide, each molecule of pyrogallol combines with 3 atoms of oxygen, and the quantity of carbonic oxide formed amounts to 2·2 per cent. of the volume of oxygen absorbed (this vol., ii, 534). With sodium hydroxide, the results are practically identical.

In presence of 3 equivalents of barium hydroxide, on the other hand, each molecule of pyrogallol absorbs only about 1 atom of oxygen, whilst with 0·67 molecule or 1·33 equivalents, the quantity of oxygen absorbed is a little less than 2 atoms per molecule of pyrogallol present. These abnormal results are probably due to the fact that the product of oxidation separates as a precipitate.

With ammonia, the results are again different. If 3 molecules are present for each molecule of pyrogallol, the absorption of oxygen is at first very rapid, but eventually becomes much slower, and a considerable time is required to reach the limit of the reaction. Four atoms of oxygen are absorbed for each molecule of pyrogallol present, but the nitrogen of the ammonia is not oxidised to nitrate, although it may possibly be converted into an azo-compound. In presence of ammonia or barium hydroxide, the proportion of carbonic oxide formed is distinctly lower than in presence of sodium or potassium hydroxide.

The chief products of oxidation in presence of potassium or sodium hydroxide are a dark brown substance soluble in water and of the composition $(C_5H_5O_4)_m$ or $C_{20}H_{20}O_{16}$, and carbonic anhydride, which at once liberated on adding an excess of an acid to the alkaline solutions, although the liquid must be heated in order to expel the whole of the gas. A dark red, crystallisable compound, $C_{20}H_{20}O_{11}$, soluble in ether and having some of the properties of purpurogallin, is formed in the early stages of oxidation, whilst another compound, $(C_4H_4O_3)_n$, or probably $C_{16}H_{16}O_{12}$, also soluble in ether, is found amongst the final products in quantity equal to about 10 per cent. of the original pyrogallol. No definite evidence was obtained of the formation of any volatile acids. The quantity of the chief product, $C_{20}H_{20}O_{16}$, amounts to about 86 per cent. of the original pyrogallol.

The compound $C_{20}H_{20}O_{11}$ differs from purpurogallin, $C_{20}H_{16}O_9$, by $2H_2O$, and the product, $C_{20}H_{20}O_{16}$, differs from it by $2H_2O + O_5$. It would seem that the several products result from the condensation of 4 molecules of pyrogallol, but probably the condensation is not direct, and a compound of a quinone character, such as trihydroxyquinone, is first formed and subsequently split up thus, $4C_6H_4O_5 = C_{20}H_{16}O_{12} + 4CO_2$, the compound, $C_{20}H_{16}O_{12}$, afterwards combining with $2H_2O$ and O_2. During the oxidation, the benzene ring breaks down, and probably is converted into a more complex cyclic compound of the same order, such as triphenylethane. C. H. B.

Derivatives of Eugenol. By F. J. POND and F. T. BEERS (*J. Amer. Chem. Soc.*, 1897, **19**, 825—831).—Two classes of unsaturated benzene derivatives which contain the group C_3H_5 joined to a benzene nucleus are known; those of the formula R·CH:CHMe yield dibromides which are converted by the action of sodium methoxide into ketones of the formula R·CO·CH_2Me, whereas those of the second class,

$R{\cdot}CH_2{\cdot}CH{:}CH_2$, do not undergo this change. In order to extend the experimental evidence for this difference in properties, the authors have examined the behaviour of isoeugenol benzylic ether. *Eugenol benzylic ether*, $CH_2Ph{\cdot}O{\cdot}C_6H_3(OMe){\cdot}CH_2{\cdot}CH{:}CH_2$, is prepared by the action of benzylic chloride on an alkaline solution of eugenol, and is a dark-coloured oil which boils and decomposes at about 235°. When it is heated with alcoholic potash, it is converted into *isoeugenol benzylic ether*, $CH_2Ph{\cdot}O{\cdot}C_6H_3(OMe){\cdot}CH{:}CHMe$, which crystallises in long, white needles melting at 48°. The *dibromide* also crystallises in white needles, and melts at 122°. When this is treated with sodium methoxide, and the oily product boiled with dilute aqueous potash, it yields the *ketone*, $CH_2Ph{\cdot}O{\cdot}C_6H_3(OMe){\cdot}CO{\cdot}CH_2Me$, which crystallises in small, white needles melting at 93°. The *oxime* crystallises in white needles melting at 118·5°, and readily yields the ketone when hydrolysed with dilute sulphuric acid.

Isoeugenol benzylic ether, therefore, behaves in a similar manner to the other propenyl derivatives of analogous constitution. A. H.

Derivatives of Aromatic β- and δ-Oxides. By KARL AUWERS (*Annalen*, 1898, **301**, 203—266).—It is scarcely possible to do justice to this paper in an abstract. In a series of recent communications (compare Abstr., 1897, i, 335), the author has followed the action of bromine on phenols and phenol-alcohols, and, among the numerous compounds described in this connection, has drawn attention to certain products which, although insoluble in alkalis, are highly active in other respects. The methods of obtaining them are frequently too irregular to throw light on their constitution; the present paper, however, develops the formulæ theoretically possible, and discusses their probability, more particularly in relation to the views recently expressed by Zincke (this vol., i, 70). As a result of this discussion, the author is led to regard the bromo-compounds in question as derivatives of oxides, which in many respects resemble aliphatic oxides; that is to say, the formula $CX\left<\begin{matrix}CY{:}CY\\CH_2{-}O\\CY{:}CY\end{matrix}\right>CH$, where X represents a halogen, and Y any substituent, is preferred by the author to Zincke's expression,

$$CMeX\left<\begin{matrix}CY{:}CY\\CY{:}CY\end{matrix}\right>CO.$$

The same considerations apply to the acetates of this type which do not dissolve in alkali. M. O. F.

New Derivatives of Dibromanhydroparahydroxy-ψ-cumylic Alcohol. By KARL AUWERS and NORMAN L. SHELDON (*Annalen*, 1898, **301**, 266—282. Compare Abstr., 1897, i, 335).—According to the views developed by Auwers regarding the constitution of dibromo-ψ-cumenol bromide and allied compounds (foregoing abstract), the substance mentioned is expressed by the formula $CBr\left<\begin{matrix}CMe{:}CBr\\CH_2{-}{-}O\\CBr{:}CMe\end{matrix}\right>CH$, and may be regarded as the bromide of dibromanhydroparahydroxy-ψ-cumylic alcohol; a preliminary account of the compounds described in this paper has already appeared (*loc. cit.*).

The *acetyl* derivative of dibromoparahydroxy-ψ-cumylic bromide, $CH_2Br<\begin{matrix}CMe:CBr\\CBr:CMe\end{matrix}>C\cdot OAc$, is obtained by heating the bromide of dibromanhydroparahydroxy-ψ-cumylic alcohol (m. p. 126°) with boiling acetic anhydride during 5 hours; it crystallises from glacial acetic acid in lustrous needles, and melts at 161°. The mother liquor contains the diacetyl derivative of dibromoparahydroxy-ψ-cumylic alcohol, which melts at 105—106°.

When the acetyl derivative is heated with absolute alcohol in sealed tubes at 100°, it is converted into the ethylic ether of dibromoparahydroxy-ψ-cumylic alcohol, $OEt\cdot CH_2<\begin{matrix}CMe:CBr\\CBr:CMe\end{matrix}>C\cdot OH$, which dissolves in alkali and melts at 86—87° (compare Auwers and Marwedel, Abstr., 1896, i, 150); the *acetyl* derivative is produced along with it, and crystallises from alcohol in slender, white needles melting at 64—66°.

Dibromoparacetoxy-ψ-cumylaniline, $NHPh\cdot CH_2<\begin{matrix}CMe:CBr\\CBr:CMe\end{matrix}>C\cdot OAc$, prepared by heating a benzene solution of the tribromacetate (m. p. 161°) with aniline (2 mols.), crystallises from petroleum in lustrous octahedra melting at 120°; hydrolysis with alcoholic alkali resolves it into *dibromoparahydroxy-ψ-cumylaniline* which melts at 134° (Auwers and Marwedel, *loc. cit.*).

The *compound*, $C_{22}H_{20}Br_4O_4$, prepared by heating an alcohol solution of the tribromacetate with sodium ethoxide (1 mol.) in a reflux apparatus, crystallises from hot petroleum in slender, lustrous needles, and melts at 175°. Alcoholic potash resolves the substance into the ethylic ether of dibromoparahydroxy-ψ-cumylic alcohol, which is also formed when the tribromacetate is warmed with alcoholic sodium ethoxide (2 mols.). Hydrogen bromide converts it into the *compound*, $C_{18}H_{16}Br_4O_2$, which crystallises from glacial acetic acid in lustrous needles, and melts at 217—220°.

When the diacetyl derivative of dibromoparahydroxy-ψ-cumylic alcohol is heated with alcoholic sodium ethoxide (1 mol.), it yields tetrabromodihydroxytetramethylstilbene (Abstr., 1896, i, 150). Under the influence of sunlight, bromine in glacial acetic acid converts the diacetyl compound into dibromopara-xyloquinone (m. p. 181—182°), diffused light causing it to yield the acetyl derivative melting at 161°; if carbon bisulphide is used in place of glacial acetic acid, the bromide of dibromanhydroparahydroxy-ψ-cumylic alcohol (m. p. 126°) is formed. The latter compound is also produced when hydrogen bromide is passed into a solution of the diacetyl derivative in glacial acetic acid at 70°, the tribromacetate (m. p. 161°) being formed at ordinary temperatures.

The *acetyl* derivative of dibromoparahydroxy-ψ-cumylic alcohol, $OH\cdot CH_2\cdot C<\begin{matrix}CMe:CBr\\CBr:CMe\end{matrix}>C\cdot OAc$, prepared from the diacetyl derivative by heating the solution in acetone and water with caustic soda (1 mol.), crystallises from petroleum in small, lustrous needles, and melts at 120—121·5°.

An isomeric tribromo-ψ-cumenol has been obtained as a bye-product

in the preparation of dibromo-ψ-cumenol bromide (Abstr., 1896, i, 423); although the melting point as originally given is 181°, later preparations melted at 175°. The *acetyl* derivative crystallises from methylic alcohol in flat, lustrous needles, and melts at 122—124°; hydrolysis regenerates tribromo-ψ-cumenol melting at 180°. M. O. F.

Mercury Compounds of Organic Bases. By LEONE PESCI (*Zeit. anorg. Chem.*, 1897, 15, 208—233).—The paper contains a concise account of the various mercury compounds of organic bases, which have at various times been prepared by the author and his pupils, and is divided into the following chapters: I. *Mercurioanilido-compounds* (compare Abstr., 1892, 1448; 1894, i, 248; 1897, i, 559; 1893, ii, 278; 1893, i, 322). II. *Mercury compounds of methylaniline* (Abstr., 1893, i, 24; 1894, i, 248). III. *Mercury compounds of dimethylaniline* (Abstr., 1894, i, 248). IV. *Mercury compounds of ethylaniline* (Abstr., 1894, i, 249). V. *Mercury compounds of diethylaniline* (Abstr., 1894, i, 249). VI. *Mercury compounds of benzylaniline* (Abstr., 1897, i, 337). VII. *Mercury compounds of acetanilide* (Abstr., 1895, i, 357, 358). VIII. *Mercury compounds of benzylamine* (Abstr., 1897, i, 36). IX. *Mercuroquinoline compounds* (Abstr., 1896, i, 186). X. *Mercuropyridine compounds* (Abstr., 1896, i, 388). XI. *Mercury a-picoline compounds* (Abstr., 1897, i, 370). XII. *Mercuropiperidine compounds* (Abstr., 1897, i, 370). XIII. *Mercurocarbamide and its salts* (Abstr., 1897, i, 328). A. W. C.

Mercury Compounds of Dimethylparatoluidine and of Paratoluidine. By LEONE PESCI (*Zeit. anorg. Chem.*, 1898, 17, 276—283).—Compounds obtained by the action of mercury salts on non-substituted anilines contain the mercury atom in the para-position, whereas the compounds of dimethylparatoluidine and of paratoluidine contain the mercury which is combined with the aromatic nucleus in the meta-position relatively to the methyl group. This is proved by the synthesis of mercury dimethylparatoluidine by heating metabromodimethylparatoluidine with ethylic acetate and sodium amalgam at 120—125° for 48 hours.

Mercuryditoluylenetetramethylmercuridiammonium compounds contain the bivalent radicle $Hg{<}{}^{C_6H_3Me\cdot NMe_2}_{C_6H_3Me\cdot NMe_2}{>}Hg$ [$Me:Hg:NMe_2 = 1:3:4$].

The *hydroxide*, $Hg(C_6H_3Me\cdot NMe_2\cdot OH)_2Hg$, obtained by allowing the acetate to remain for 24 hours with concentrated potassium hydroxide, crystallises in colourless, microscopic needles, sinters at 114°, melts at 117°, is only sparingly soluble in cold water, but very easily in methylic alcohol or benzene. The *acetate*, obtained by adding an alcoholic solution of dimethylparatoluidine to a solution of mercury acetate in dilute alcohol, crystallises in colourless, lustrous needles, melts at 131·5°, is easily soluble in methylic alcohol, less so in ethylic alcohol, and insoluble in water. The *nitrate*, obtained by treating an alcoholic solution of the acetate with calcium nitrate, crystallises in colourless needles and melts at 131°. The *chloride* crystallises in slender needles and melts at 159—159·5°; the *bromide* in lustrous

needles melting at 149—150°, and the *iodide* in yellow needles melting at 126°.

Mercurydimethylparatoluidine, $Hg(C_6H_3Me{\cdot}NMe_2)_2$, obtained by the action of sodium thiosulphate on the above hydroxide suspended in water, crystallises from boiling alcohol in colourless, lustrous leaflets, melts at 60°, is easily soluble in benzene, and when treated with mercury iodide, bromide, chloride, and acetate, yields the salts described above. The mercurydimethylparatoluidine obtained by synthesis from metabromodimethylparatoluidine is in every respect identical with this product.

Mercuryditoluylenemercuridiammonium compounds containing the radicle $Hg(C_6H_3MeNH_2)_2Hg$ [Me : Hg : NH_2 = 1 : 3 : 4].

The *hydroxide*, obtained by the action of potassium hydroxide on the acetate, crystallises in yellowish leaflets, begins to decompose at 120°, melts at 212—213°, has a strongly alkaline reaction, and is insoluble in most solvents. The *acetate*, obtained by the action of mercury acetate on paratoluidine, crystallises in leaflets, melts at 184°, and is easily soluble in benzene, alcohol, or ether, but insoluble in water. The *chloride* crystallises in prisms and melts at 170°.

Mercuryparatoluidine, $Hg(C_6H_3Me{\cdot}NH_2)_2$, obtained by heating the preceding hydroxide with sodium thiosulphate, crystallises from boiling alcohol in four-sided leaflets, melts at 156°, and is insoluble in most of the ordinary solvents. It cannot be prepared from the metabromoparatoluidine, but most probably has the same constitution as the preceding mercury dimethylparatoluidine. E. C. R.

Electro-synthesis of Anhydroparamidobenzylic Alcohol. By Walther Löb (*Ber.*, 1898, **31**, 2037—2038).—The electrolytic reduction of a mixture of nitrobenzene and formaldehyde in acid solution yields two different products according to the current density at the cathode. With a high current density, anhydroparahydroxylaminobenzylic alcohol is obtained, and with a low density and at low temperatures the substance formed is produced from 3 molecules of formaldehyde and 2 of nitrobenzene by reduction.

Under special conditions, anhydroparamidobenzylic alcohol may be obtained. One part of formaldehyde (in 40 per cent. solution) and 25 parts of concentrated hydrochloric acid are added to a solution of 1 part of nitrobenzene in 40 parts of alcohol, and the mixture reduced by the use of a platinum cathode, the current density of which is $ND_{100} = 0{\cdot}5$ ampère, whilst the temperature is kept at about 12°. The clear, reddish-yellow solution, when freed from alcohol and rendered alkaline, yields anhydroparamidobenzylic alcohol. J. J. S.

Some Amidoketones. By Hugh Ryan (*Ber.*, 1898, **31**, 2129—2133). —*Ethylic metaxylylacetoacetate*, $C_6H_4Me{\cdot}CH_2{\cdot}CH(COMe){\cdot}COOEt$, obtained by the action of metaxylylic bromide on the sodium compound of ethylic acetoacetate, is a yellowish oil which distils at 195° under a pressure of 36 mm.; it dissolves slowly in dilute alkali, and yields a crystalline sodium salt when shaken with strong soda. By acting on this compound with nitrous acid under varied conditions, *isonitrosometaxylylacetic acid*, $C_6H_4Me{\cdot}CH_2{\cdot}C(:NOH){\cdot}COOH$, and *isonitroso-*

metaxylylacetone, $C_6H_4Me\cdot CH_2\cdot C(\colon N\cdot OH)\cdot COMe$, are obtained. The former crystallises in colourless needles and melts at 139°; its *silver* salt has the composition $C_{10}H_{10}AgNO_3$. The latter dissolves readily in ether, alcohol, and benzene, forms aggregates of needles, and melts at 54—55°; its solution in alkalis is yellow. *Amidometaxylylacetone*, $C_6H_4Me\cdot CH_2\cdot CH(NH_2)\cdot COMe$, is prepared from the isonitrosoketone by reduction with tin and hydrochloric acid; the hydrochloride, $C_{11}H_{15}NO,HCl$, is crystalline, melts at 150—151°, and reduces warm Fehling's solution; the *stannichloride*, $(C_{11}H_{15}NO)_2,H_2SnCl_6$, is colourless, and melts at 177—178°; the *platinochloride*, $(C_{11}H_{15}NO)_2,H_2PtCl_6$, forms yellow crystals and melts at 187°; the *picrate*, $C_{11}H_{15}NO,C_6H_3N_3O_7$, melts at 87°. The hydrochloride of the foregoing base, when treated with potassium thiocyanate, yields *metaxylylmethylimidazolylmercaptan*, $\begin{array}{l} C_8H_9\cdot C{-}{-}{-}N \\ \qquad \| \\ \quad\ CMe\cdot NH \end{array}\!\!>\!C\cdot SH$ or $\begin{array}{l} \qquad CMeN \\ \qquad \| \\ C_8H_9\cdot C{-}NH \end{array}\!\!>\!C\cdot SH$, which forms microscopic crystals melting at 267°; if potassium cyanate is employed, *metaxylylmethylimidazolone*, $\begin{array}{l} C_8H_9\cdot C{-}{-}{-}NH \\ \qquad \| \\ \quad\ CMe\cdot NH \end{array}\!\!>\!CO$, melting at 265°, is produced.

Paramethyl-α-phthalimidoacetophenone, $C_6H_4Me\cdot CO\cdot CH_2\cdot N\colon C_8H_4O_2$, is prepared by heating paramethyl-α-chloracetophenone with potassium phthalimide; it forms octahedra-like crystals, dissolves readily in hot glacial acetic acid, and sparingly in alcohol and ether; it is insoluble in water, and melts at 175—176°; its phenylhydrazone,

$$C_6H_4Me\cdot C(\colon N_2\cdot HPh)\cdot CH_2\cdot N\colon C_8H_4O_2,$$

forms beautiful, yellow needles, and melts at 154°. The corresponding *phthalamic acid*, $C_6H_4Me\cdot CO\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot COOH$, melts at 165° and gives a blue, crystalline *copper* salt and a white, crystalline *silver* salt, $C_{17}H_{14}AgNO_4$; when boiled with hydrochloric acid, it is hydrolysed, yielding phthalic acid and *paramethyl-α-amidoacetophenone hydrochloride*, $C_6H_4Me\cdot CO\cdot CH_2\cdot NH_2,HCl$. This crystallises from alcohol in colourless needles, and melts at 206°, forming a red liquid; its solution instantly reduces Fehling's solution, and, on treatment with alkali, yields the free base, which at once reddens and decomposes. The *aurochloride* of the base, $C_9H_{11}NO,HAuCl_4$, crystallises in long needles melting at 167°; the *platinochloride*, $(C_9H_{11}NO),H_2PtCl_6$, crystallises from hot water in long prisms melting at 206°; the picrate, $C_9H_{11}NO,C_6H_3N_3O_7$, crystallises from alcohol in yellow needles melting at 176°. A. L.

Action of Amines on Acylimido-ethers: Acylamidines. By Henry L. Wheeler and Percy T. Walden (*Amer. Chem. J.*, 1898, 20, 568—576).—In the production of the acylamidines from acylimido-ethers (compare this vol., i, 185), it is probable that an additive product is first formed, which is subsequently decomposed; thus from benzoylbenzimidomethylic ether and ammonia, the derivative $OMe\cdot CPh(NH_2)\cdot NHBz$ would be first produced, and its decomposition would give rise to a substance having one of the two formulæ,

$$\text{I. } NH\colon CPh\cdot NHBz, \text{ or II. } NH_2\cdot CPh\colon NBz.$$

The benzoylbenzamidine actually obtained by the author in this

reaction is identical with the substance to which Pinner attributed the first of these formulæ, since it was readily converted into dibenzamide by the loss of ammonia. This decomposition, however, cannot be looked on as satisfactorily establishing the constitution of Pinner's benzoylbenzamidine; for assuming that the hydrolysis takes place through an initial addition of $1H_2O$, the same additive product, $NH_2\cdot CPh(OH)\cdot NHBz$, would be formed from both the amidines I and II, and both the latter could therefore give rise to dibenzamide and ammonia. That such decompositions afford no clue to the structure of amidines is shown by the behaviour of the similarly constituted benzoylbenzimido- and benzoylphenylacetamido-ethylic ethers on hydrolysis; whereas the former, $OEt\cdot CPh\colon NBz$, gives rise to dibenzamide and alcohol, the latter, $OEt\cdot C(C_7H_7)\colon NBz$, yields benzamide and phenylethylic acetate (*loc. cit.*).

Beckmann and Sandel (Abstr., 1897, i, 564) have stated that benzoylbenzimide chloride, $NBz\colon CPhCl$, unites readily with ammonia and primary amines to form amidines, but that it does not combine with secondary amines; the authors find similarly that the acylimido-ethers are not acted on by secondary bases.

Benzoylbenzamidine, prepared by warming an alcoholic solution of benzoylbenzimidopropylic ether with aqueous ammonia, is identical with the substance obtained by Pinner on dissolving benzonitrile in fuming sulphuric acid; both melt at 100—101°, not at 106° as stated by Pinner. The *hydrochloride*, $C_{14}H_{12}N_2O,HCl$, melts at about 190°, and is decomposed by water; the *platinochloride*, $(C_{14}H_{12}N_2O)_2,H_2PtCl_6$, on being heated, darkens at 225—230°, and melts at 240°.

Benzoylethylbenzamidine, prepared from ethylamine and benzoylbenzimidopropylic ether, melts at 88°, and is probably identical with the substance obtained by Lossen (Abstr., 1892, 51) from ethylbenzamidine and benzoic chloride.

Benzoylphenylbenzamidine, prepared from benzoylbenzimidoethylic ether and aniline, melts at 143°, and has been described by Beckmann and Sandel (*loc. cit.*); methylaniline and ethylaniline do not interact with benzoylbenzimidoethylic ether.

Acetylphenylbenzamidine, $C_{15}H_{14}N_2O$, prepared from acetylbenzimidoethylic ether and aniline, separates from alcohol in colourless crystals, and melts at 138·5°; *acetylparatolylbenzamidine* melts at 136·5°, whilst *acetylmetachlorophenylbenzamidine* melts at 128—129°. 1 : 3 : 4-*Xylylbenzamidine* is formed when 1 : 3 : 4-xylidine is left in contact with acetylbenzimidoethylic ether, the acetyl group being removed; it crystallises from light petroleum in long, colourless needles, and melts at 106°. *Acetyl-β-naphthylbenzamidine*, from β-naphthylamine and acetylbenzimidoethylic ether, melts at 137°; and *propionylphenylbenzamidine* from aniline and the corresponding imido-ether, at 138°. Attempts to prepare normal butyrylbenzamidine by dissolving butyrylbenzimidoethylic ether in dilute alcoholic ammonia failed, benzamide being formed; the same result was obtained by similarly treating acetyl- and propionyl-benzimido-ethers,

Normal butyrylphenylbenzamidine, prepared from butyrylbenzimidoethylic ether and aniline, separates from alcohol in colourless prisms, and melts at 137°. W A. D.

Aromatic Azomethine Compounds. By RICHARD MÖHLAU (*Ber.*, 1898, **31**, 2250—2261. Compare Abstr., 1893, i, 470).—The compounds produced by the action of aromatic aldehydes on primary aromatic bases possess a constitution somewhat analogous to that of azo-derivatives, and also resemble these in the possession of tinctorial properties. These properties are due to the chromophoric group –N⁚CH–, which corresponds with the azo-group in azo-colours. Azomethine compounds, analogous to basic and acidic azo-derivatives, have already been prepared (Abstr., 1895, i, 214 and 221), whilst the following are described for the first time.

Paramidobenzylidenedimethylparaphenylenediamine,

$$NH_2\cdot C_6H_4\cdot CH⁚N\cdot C_6H_4\cdot NMe_2,$$

is termed by the author *anhydroparamidobenzaldehydeparamidodimethylaniline*, similar names being given to the other compounds described. It is obtained by heating together a hydrochloric acid solution of paramidobenzaldehyde and paramidodimethylaniline; the free base crystallises from dilute methylic alcohol in yellow leaflets melting at 191—192°, and it is hydrolysed by acids, yielding its components.

Paradiethylamidobenzylidenedimethylparaphenylenediamine,

$$NEt_2\cdot C_6H_4\cdot CH⁚N\cdot C_6H_4\cdot NMe_2,$$

produced on heating together paraformaldehyde, diethylaniline, and nitrosodimethylaniline in presence of hydrochloric acid, crystallises from methylic or ethylic alcohol in yellow prisms melting at 140—141°. The *hydrochloride* forms red, prismatic crystals with a steel-blue reflex.

Bis-paradimethylamidobenzylidene-paraphenylenediamine,

$$NMe_2\cdot C_6H_4\cdot CH⁚N\cdot C_6H_4\cdot N⁚CH\cdot C_6H_4\cdot NMe_2,$$

melts at 190°. The corresponding *ethyl* compound, obtained by adding nitroso-dimethylaniline hydrochloride to a solution of paraformaldehyde and diethylaniline in hydrochloric acid, and subsequently treating the product with alkalis, crystallises from dimethylaniline in golden-yellow needles, and melts at 206·5—207·5°. The *hydrochloride* forms red needles with a steel blue reflex, and contains $7H_2O$.

Bis-parethylamidometatolylidene-paraphenylenediamine,

$$NHEt\cdot C_7H_6\cdot CH⁚N\cdot C_6H_4\cdot N⁚CH_2\cdot C_7H_6\cdot NHEt,$$

is obtained by the above reaction from ethylorthotoluidine, which appears to behave like a tertiary aromatic amine; the condensation product crystallises from dimethylaniline in dark yellow, lustrous prisms, and melts at 234—235°. Several phenolic azomethine derivatives corresponding with hydroxy-azo-compounds are already known (Abstr., 1888, 50, and 1893, i, 273), and the following are obtained by condensing paranitrobenzaldehyde with the three amidonaphthols in alcoholic solution in the presence of acetic acid.

1 : 4-*Paranitrobenzylideneamidonaphthol* crystallises from alcohol in scarlet leaflets, and melts at 171°; it dissolves in aqueous alkalis, forming a cherry-red solution, and with alcoholic soda it develops a deep violet coloration. The 1 : 2-*compound* forms scarlet prisms with a golden lustre, and melts at 174°; aqueous solutions of its salts are red, whilst their alcoholic solutions are violet. The 2 : 1 *compound*, which

crystallises from alcohol in orange needles and melts at 187°, is insoluble in aqueous alkalis, but develops a violet coloration with alcoholic soda.

These three isomerides are all hydrolysed into their components when their solutions in concentrated sulphuric acid are diluted with water. Schiff (Abstr., 1882, 303) has previously obtained azomethine compounds corresponding with azocarboxylic acids. The azomethine analogues of "Alizarine yellow R" and "Alizarine yellow 2G" are now described.

Paranitrobenzylidene-5-amidosalicylic acid results from the condensation of 1 : 2 : 5-amidosalicylic acid with paranitrobenzaldehyde in alcoholic solution; it crystallises from dilute alcohol in golden-yellow needles, and decomposes at 217—218°. It closely resembles its azo-analogue. The *metanitro*-compound, prepared by substituting metanitrobenzaldehyde for its para-isomeride, crystallises in pale yellow needles, and decomposes at 252°. The *orthonitro*-compound, obtained from orthonitrobenzaldehyde, forms lemon-yellow needles, and decomposes at 221°. In the case of these three azomethine derivatives, it is found that their basic alkali salts have the same colour as the normal salts of the corresponding azo-colours. G. T. M.

Formation of Salts and Hydrates of Azophenol. By JOHN T. HEWITT, T. S. MOORE, and A. E. PITT (*Ber.*, 1898, 31, 2114—2123. Compare Abstr., 1894, i, 123; 1895, i, 353, &c.).—*Orthobromobenzeneazophenol*, $C_6H_4Br\cdot N_2\cdot C_6H_4\cdot OH$, may be obtained in a hydrated form, as well as in an anhydrous state. The former, $C_{12}H_9BrN_2O,\frac{1}{2}H_2O$, is yellow, melts at 85°, and yields the anhydrous form when gently warmed. The latter is red, and melts at 97°; it is readily soluble in acetone and in nitrobenzene, but dissolves only sparingly in light petroleum. The *hydrochloride* is dark red, and melts between 116° and 127°, hydrogen chloride being evolved; the *acetate*, which forms bright yellow crystals melting at 89°, dissolves in the ordinary solvents with the exception of light petroleum. The *benzoate* forms orange crystals, and melts at 122—123°; the *benzenesulphonate* melts at 69°.

Parabromobenzeneazophenol, $C_6H_4Br\cdot N_2\cdot C_6H_4\cdot OH$, crystallises from toluene in brownish-red needles melting at 157°. The *hydrochloride* is bright red, melts at 171—177°, and does not afford a hydrated azophenol on treatment with water. The *acetate* crystallises from ethylic acetate in orange needles melting at 158°. The *benzoate* crystallises in beautiful, bright yellow leaflets, and melts at 166°, whilst the benzenesulphonate forms bright yellow crystals, and melts at 136°.

Metatolueneazophenol hydrochloride, when decomposed with water, yields a *hydrate*, $(C_{13}H_{22}N_2O)_2,H_2O$, which may also be obtained by dissolving the anhydrous form in sulphuric acid, and then adding water; it forms small, bright yellow leaflets, and darkens in colour when heated at 90°.

Orthophenetoilazophenol hydrochloride, $C_{14}H_{14}N_2O_2,HCl$, is dark red, and melts at 125—131°; it yields only the anhydrous modification of the azophenol, and therefore differs in this respect from the other ortho-substituted azophenols which have been examined.

The *benzoate* separates from alcohol in red needles, and melts at 99°; the *benzenesulphonate* crystallises from boiling alcohol in large, red needles, and melts at 84°.

Metaphenetoilazophenol hydrochloride is deep rose-red, and melts at 140—150°; it yields a hydrated azophenol, $(C_{14}H_{14}N_2O_2)_2 + H_2O$, which melts at 89—91°. The *benzenesulphonate* separates from dilute alcohol in aggregates of bright-red needles, and melts at 77°.

Paraphenetoilazophenol hydrochloride is of a carmine colour, and decomposes at 132—160°; when treated with water, it yields a hydrated modification, $C_{14}H_{14}N_2O_2 + H_2O$, of the parent substance, which melts at 105—110°; this melting point is in close agreement with that observed by Riedel (D.R.-P. 48543), and accounts for the difference between the melting points given by him and by Jacobson (Abstr., 1896, i, 27), who was dealing with the anhydrous form. The *acetate* of paraphenetoilazophenol forms yellow leaflets and melts at 119°. The *benzoate* forms brownish-red crystals, and melts at 127°, whilst the *benzenesulphonate* separates from boiling alcohol in large, brown leaflets which melt at 105°.

Orthonitrobenzeneazophenol does not form a stable hydrochloride, a fact probably due to the weakening of the basicity produced by a strongly negative group in the ortho-position, and not to any steric hindrance to chemical action. *Metanitrobenzeneazophenol hydrochloride*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH,HCl$, melts at 167—171°; *paranitrobenzeneazophenol hydrochloride* is dark-red, and melts and slowly decomposes at 158—167·5°. Neither of these two compounds yields a hydrated azophenol on treatment with water.

The authors finally draw some general conclusions, for which the original paper must be consulted. A. L.

Electro-synthesis of Mixed Azo-compounds. By WALTHER LÖB (*Ber.*, 1898, 31, 2201—2205).—Kauffmann and Hof have shown that when metanitrobenzaldehyde is electrolytically reduced in alkaline solution, the chief product is metazobenzoic acid together with a small quantity of metazobenzylic alcohol. They sought to explain this preponderance of acid by supposing that the nitrobenzylic alcohol, under the action of the alkali, is converted into azoxybenzylic alcohol and azoxybenzoic acid according to the equation $8NO_2 \cdot C_6H_4 \cdot CH_2 \cdot OH = 3(COOH \cdot C_6H_4)_2N_2O + (OH \cdot CH_2 \cdot C_6H_4)_2N_2O + 6H_2O$, and that these, on electrolysis, yield the corresponding azo-compounds. This supposition is considered by the author to be untenable, since no trace of the sparingly soluble azoxy-compounds could be detected during the electrolysis. It is also shown that the azo-acid consists of only a small amount of metazobenzoic acid, the chief product being a mixed azo-derivative, $COOH \cdot C_6H_4 \cdot N \colon N \cdot C_6H_4 \cdot CH_2 \cdot OH$.

Direct experiment has shown that when equivalent quantities of two nitro-derivatives in alkaline solution are reduced at the cathode, a mixed azo-compound is always formed. Under suitable conditions, the positions of the substituting groups are without influence, so that practically any azo-compounds may be obtained by this method, whereas Griess's method yields only amido- or hydroxy-derivatives with the substituting groups in the para- or ortho-position.

It has not been found possible to electrolytically reduce nitrophenols to azophenols.

If lead electrodes are employed, the reduction often proceeds as far as the formation of hydrazo-derivatives; the best yield of azo-compound is obtained with platinum or mercury electrodes.

Exo-hydroxytoluenemetazometabenzoic acid,

$$COOH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot CH_2\cdot OH,$$

obtained by the reduction of metanitrobenzaldehyde, crystallises from alcohol in yellow plates melting at 182—183°, and is readily soluble in alcohol or ether, but insoluble in water.

Toluenepara-azometabenzoic acid, $C_6H_4Me\cdot N_2\cdot C_6H_4\cdot COOH$, from paranitrotoluene and metanitrobenzoic acid, melts at 192° and is readily soluble in ether or alcohol.

Metasulphobenzeneazometabenzoic acid, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot COOH$, from nitrobenzenesulphonic acid and metanitrobenzoic acid, crystallises in yellow plates which decompose when heated. It is insoluble in ether, but dissolves readily in water or alcohol.

Paramidobenzeneazometabenzoic acid, $NH_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot COOH$, from paranitraniline and metanitrobenzoic acid, crystallises in yellowish-red needles, is readily soluble in alcohol, sparingly in hot water, and insoluble in ether.

Paramidosulphobenzeneazometabenzoic acid,

$$SO_3H\cdot C_6H_3(NH_2)\cdot N_2\cdot C_6H_4\cdot COOH,$$

forms yellowish-red crystals, dissolves in water, and gives, on addition of acids, a blood-red coloration, and of alkalis, an intense yellow coloration.

Paradimethylamidobenzeneazometabenzoic acid, obtained from metanitrobenzoic acid and paranitrodimethylaniline, has already been described by Griess. J. J. S.

Additive Compounds of Diazonium-haloids with Phenols and with Acetic Acid. By ARTHUR R. HANTZSCH (*Ber.*, 1898, **31**, 2053—2057).—Diazonium haloids readily dissolve in both phenol and acetic acid, and in several cases well-defined, crystalline additive compounds can be obtained on the addition of benzene. All these additive compounds are extremely unstable and are immediately decomposed into their constituents by water, alcohol, or ether. The yellow phenol derivatives are more stable than the corresponding acetic acid compounds; similar additive compounds are formed with formic acid, but they cannot be obtained in a crystalline condition. Homologues of phenol, the cresols, for example, also yield crystalline products; resorcinol and β-naphthol, on the other hand, at once combine to yield azo-dyes. No additive compounds can be obtained with ethylic acetoacetate or with ethylic malonate, although many diazonium chlorides are soluble in these ethereal salts. Diazonium haloids appear to form additive compounds most readily, diazonium nitrates not so readily, and the sulphates not at all.

Diazonium chloride or bromide dissolves in crystallised phenol (2 mols.) forming a red oil, but no crystalline derivatives are formed.

Parabromodiazonium chloride phenate, $C_6H_4Br\cdot N_2Cl,2PhOH$, is most

easily obtained by dissolving the diazo-salt (1 gram) in a mixture of phenol (2·5 grams) and benzene (5 grams); on the addition of light petroleum, a reddish oil separates which rapidly sets to a mass of yellow needles. It melts at 83—85°, but decomposes at the same time; although not soluble in benzene, it dissolves in a mixture of benzene and phenol. *Parabromodiazonium nitrate phenate*, obtained in a similar manner, also crystallises in yellow needles, melting and decomposing at 55—60°. *Paratoluenediazonium chloride* and *pseudocumenediazonium chloride phenates* could not be obtained in a solid form. *Tribromodiazonium bromide phenate* crystallises in yellow needles, and is even less stable than the monobromo-compound.

Parabromodiazonium chloride acetate, $C_6H_4Br·N_2Cl,C_2H_4O_2$, is obtained when benzene is added to a solution of parabromodiazonium chloride (1 gram) in glacial acetic acid (1 gram); it is first deposited as an oil, but quickly solidifies to a mass of colourless needles; it is extremely unstable and readily loses acetic acid.

Parabromodiazonium bromide acetate, $C_6H_4Br·N_2Br,C_2H_4O_2$, also crystallises in colourless needles and decomposes between 85° and 90°; after remaining for some six days in a desiccator, it is completely resolved into its constituents. Tribromodiazonium bromide does not combine with acetic acid, and bromodiazonium nitrate yields only an oily additive compound.

In this connection, the author mentions the results obtained by Ley on examining the cryoscopic behaviour of diazonium salts in acetic acid, and compares these with similar results obtained with lithium chloride. J. J. S.

Derivatives of Amidoazobenzene. By MARIO BETTI (*Gazzetta*, 1898, **28**, i, 241—245).—*Chloralamidoazobenzene*,

$$NPh:N·C_6H_4·NH·CH(OH)·CCl_3,$$

obtained by heating a mixture of chloral and amidoazobenzene with a little alcohol on the water bath, crystallises in yellow scales melting at 127°, and is converted into acetamidoazobenzene on boiling with acetic anhydride. *Butylchloralamidoazobenzene*,

$$NPh:N·C_6H_4·NH·CH(OH)·CCl_2·CHMeCl,$$

prepared in an analogous manner, crystallises in yellow scales melting at 96—97°. *Furfurylideneamidoazobenzene*, $NPh:N·C_6H_4·N:CH·C_4OH_3$, obtained by heating furfuraldehyde with amidoazobenzene, crystallises in red needles melting at 129—130°. *Salicylideneamidoazobenzene*, $NPh:N·C_6H_4·N:CH·C_6H_4·OH$, prepared by heating salicylaldehyde with amidoazobenzene, crystallises in red scales melting at 155°. *Formylamidoazobenzene*, $NPh:N·C_6H_4·NH·CHO$, is prepared from ethylic formate and amidoazobenzene, and is a yellow, crystalline substance melting at 162°. *Allylamidoazobenzenethiocarbamide*,

$$NPh:N·C_6H_4·NH·CS·NH·C_3H_5,$$

obtained by heating amidoazobenzene with mustard oil, crystallises in yellow needles melting at 133—134°. W. J. P.

Preparation of Phenylamidoazobenzene and Azophenine. By T. LYNTON BRIGGS (*J. Soc. Chem. Ind.*, 1895, **14**, 851—852).—The following method of preparing phenylamidoazobenzene on the large scale gives better results and is more rapid than the process described

by Witt (*Ber.*, 1879, **12**, 259); it is analogous to the latter's method of preparing tropæoline OO (potassium phenylamidoazobenzenesulphonate). Diphenylamine (34 parts) is dissolved in phenol, and after cooling as much as possible without allowing crystallisation to take place, agitated during several hours with an ice cold solution of diazobenzene chloride; the latter is prepared by the interaction of 20 parts of aniline, 14·5 parts of sodium nitrite, and 44 parts of dilute hydrochloric acid (sp. gr. = 1·162). The crude phenylamidoazobenzene is freed from phenol by agitation with warm concentrated caustic soda.

Azophenine can be conveniently prepared by heating phenylamidoazobenzene (50 parts) with aniline (100 parts) and aniline hydrochloride (5 parts) during 24 hours at 50°. If a larger quantity (60 parts) of aniline hydrochloride be employed, and the mixture heated during the first few hours at 100—130°, subsequently at 160—180° during 24 hours, the dye-stuff "induline G O" is obtained. W. A. D.

Action of Nitric Peroxide on Nitrosophenols. By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1898, **28**, i, 305—310).—Nitric peroxide acts on quinoneoximes or nitrosophenols with formation of dinitrophenols in which the two nitro-groups are in the ortho- and para-positions relatively to the hydroxyl group. Ethereal solutions of the nitroso-compounds and nitric peroxide were used in the work.

Nitrosophenol, under these conditions, yields 2 : 4-dinitrophenol, and nitro-orthocresol, the 3 : 5-dinitro-orthocresol melting at 85—86°; nitrosothymol similarly gives the 3 : 5-dinitro-1-propyl-2-phenol melting at 55°, whilst β-naphthaquinoneoxime yields Martius's 2 : 4-dinitro-1-naphthol melting at 138°. W. J. P.

Hydroxylamidoximes. A New Series of Hydroxylamine Derivatives. By HEINRICH LEY (*Ber.*, 1898, **31**, 2126—2129).—Hydroxylamine reacts with the chlorides of hydroxamic acids in accordance with the equation

$$R\cdot CCl\colon N\cdot OH + H_2N\cdot OH = OH\cdot NH\cdot CR\colon N\cdot OH + HCl.$$

Hydroxylamine hydrochloride is dissolved in the smallest possible amount of alcohol, and mixed with the calculated quantity of sodium ethoxide, excess of the latter being carefully avoided; the solution is then freed from sodium chloride by filtration, mixed with an ethereal solution of the chloride of benzhydroxamic acid, allowed to remain for 12 hours, and evaporated in a vacuum. The residue is now shaken with ether, which dissolves the new oxime, and, on evaporation, leaves it as an oil which crystallises when triturated with a few drops of benzene.

The product obtained by chlorinating benzaldoxime in chloroform solution, after being freed from hydrogen chloride by exposure in a vacuum desiccator containing potash and paraffin, may be used instead of the purified chloride in the above reaction.

Benzenylhydroxylamidoxime, $OH\cdot NH\cdot CPh\colon N\cdot OH$, crystallises from light petroleum and ethylic acetate in beautiful, shining, tabular crystals, and dissolves readily in alcohol, ether, benzene, and water, but is insoluble in light petroleum; it decomposes at 115°, evolving a large quantity of gas. Like Bamberger's azohydroxamides and the author's oxyamidine (this vol., i, 252), its solution in alcohol or water gives a

blue coloration with ferric chloride, and possesses weak acidic properties, giving a *copper* salt, $C_{14}H_{14}N_4O_4Ca$, which crystallises in microscopic leaflets. Its aqueous solution gives a pure yellow precipitate with mercuric chloride, and a blue coloration with ammonia and alkalis. The presence of the NHOH group in the molecule is shown by the fact that it instantly reduces ammoniacal silver nitrate and Fehling's solution in the cold.

When the substance is mixed with cold acetic anhydride, a vigorous evolution of gas occurs and benzonitrile is formed; this behaviour would lead one to suppose that it possesses the structure
$$\begin{array}{l} Ph\cdot C\cdot NH\cdot OH \\ \quad\ \ \| \\ \quad\ \ N\cdot OH \end{array}$$
analogous to that of the syn-oximes. A. L.

Tinctorial Reactions. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], **17**, 449—455).—Weighed quantities of wool were treated with water, very dilute hydrochloric acid, and solutions of various basic colouring matters, the residual liquids being afterwards examined and the electrical conductivity determined in each case. The liquid obtained by boiling wool with water, or by digestion therewith at 75°, is neutral to litmus and phenolphthalein; it contains ammonia and, apparently, other nitrogenous basic substances, besides salts of lime and traces of oxide of iron, alumina, magnesia, potash, and soda. The amount of dissolved matter and the conductivity of the liquid depend on the time and temperature of the extraction, and on the previous washings of the wool. When wool is digested at 75° with $\frac{1}{2000}$ normal hydrochloric acid, the liquid acquires a conductivity equal to that of solutions of the chlorides of ammonium or calcium of equivalent strength, and it is found, in fact, that the whole of the acid remains in solution and is neutralised by the basic substances extracted from the wool. If, on the other hand, the wool is first extracted with water, and hydrochloric acid is then added to the filtered liquid, the conductivity of the liquid is but little less than that due to the acid alone. When digested with $\frac{1}{2000}$ normal solutions of magenta, chrysoidin, and vesuvin, the colour-base is fixed by the wool, whilst the acid remains in solution in combination with the basic substances extracted from the fibre. The conductivity of the exhausted dye-bath is accordingly found to be equal to that of the liquid obtained by the action on wool of $\frac{1}{2000}$ normal acid alone. The results of these experiments are in accordance with Knecht's theory that in dyeing with basic dyes there is a true double decomposition between the colouring matter and the substance of the fibre. N. L.

Action of Nitric Acid on Benzamide, Phenylacetamide, and Phenylpropionamide. By H. J. TAVERNE (*Rec. Trav. Chim.*, 1897, **16**, 253—256. Compare Abstr., 1897, i, 619, and this vol., i, 588).—The nitration was effected at low temperatures, and in each case 1 gram of the amide was added, little by little, to 5 grams of pure nitric acid cooled by ice cold water, and the mixture then poured into 10 times its weight of iced water. Benzamide gave, as the only product, metanitrobenzamide; phenylacetamide gave paranitrophenylacetamide, melting at 191°, and phenylpropionamide gave the *paranitro*-derivative, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$; this crystallises from its hot aqueous

solution in light, glistening needles, melting at 174—175°, is readily soluble in ether or alcohol, and dissolves but sparingly in benzene or chloroform. J. J. S.

The So-called Phenylhydantoic Acids. By RIZZO NICCOLÒ (*Gazzetta*, 1898, **28**, i, 356—370).—The substance obtained by Jäger (*J. pr. Chem.*, 1877, [ii], **16**, 17, 29) from aniline, ammonium thiocyanate and chloracetic acid is not a phenylhydantoic acid but a carbaminethioglycollanilide, $NH_2\cdot CO\cdot S\cdot CH_2\cdot CO\cdot NHPh$; contrary to Jäger's statement, it is hydrolysed by water, yielding ammonia, carbonic anhydride, and *thioglycollanilide*, $SH\cdot CH_2\cdot CO\cdot NHPh$. The latter crystallises in needles melting at 106—107°, has the normal molecular weight in freezing acetic acid, and is soluble in water and organic solvents; it must be prepared in an atmosphere of hydrogen sulphide, because its solution oxidises in the air, yielding *dithiodiglycollanilide*, $S_2(CH_2\cdot CO\cdot NHPh)_2$, which melts at 165°.

Thiodiglycollanilide, $(NHPh\cdot CO\cdot CH_2)_2S$, obtained by passing a current of hydrogen sulphide through a solution of chloracetanilide in alcoholic ammonia, crystallises in white needles melting at 160—161°; it is insoluble in water, and has the normal molecular weight in boiling benzene or acetic acid.

On treating thioglycollanilide or carbaminethioglycollanilide with sodium methoxide and methylic iodide, *methylthioglycollanilide*, $SMe\cdot CH_2\cdot CO\cdot NHPh$, is obtained; it crystallises in needles melting at 80°, or in scales melting at 76°. On boiling carbaminethioglycollanilide with aniline, the symmetrical diphenylcarbamide melting at 235° is produced.

On heating a solution of chloracetamide, phenylthiourethane, and soda in much alcohol, *phenylthiourethaneacetamide*,

$$NH_2\cdot CO\cdot CH_2\cdot S\cdot C(OEt)\!:\!NPh,$$

is obtained; it crystallises in colourless needles and melts at 93—94°. This substance could not be converted into an isomeride of Jäger's compound, but yields phenylthiocarbamide glycollide, $CO<\begin{matrix}NPh\cdot CO\\ S\text{——}CH_2\end{matrix}$, on hydrolysis.

On boiling ammonium thiocarbamate with chloracetanilide in alcoholic solution, thiodiglycollanilide is obtained; the same compound is produced on boiling chloracetanilide and xanthogenamide with soda in alcoholic solution. Barium or ammonium thiocyanate reacts with chloracetanilide and soda in alcoholic solution, yielding thiocyanoacetanilide; attempts to synthesise Jäger's compound from this substance were also unsuccessful. W. J. P.

Some Aromatic Acetals and Aldehydes. By EMIL FISCHER and ERWIN HOFFA (*Ber.*, 1898, **31**, 1989—1998. Compare this vol., i, 311).—Aromatic aldehydes of the type of benzaldehyde give only a small yield of an acetal when treated with dilute alcoholic hydrogen chloride, unless a strongly negative group is present in the nucleus. Aldehydes in which the aldehyde group is not directly united with the aromatic nucleus, on the other hand, can be converted in this way into acetals almost as readily as the fatty aldehydes. *Phenylacetaldehydedimethylacetal*, $CH_2Ph\cdot CH(OMe)_2$, is readily formed by the action

of methylic alcohol containing 1 per cent. of hydrogen chloride on phenylacetaldehyde. It boils at 219—221° (corr.), has a specific gravity = 1·0042 at 18°, and does not possess a characteristic odour.

Cinnamaldehydedimethylacetal, CHPh:CH·CH(OMe)$_2$, has been previously described, and has also been prepared by Claisen by the aid of formimidoether (this vol., i, 421). It is converted by reduction with sodium and alcohol into *hydrocinnamaldehydedimethylacetal*, CH$_2$Ph·CH$_2$·CH(OMe)$_2$, which is, however, best prepared in a pure state from hydrocinnamaldehyde, and then boils at 240—241° (corr.), undergoing a very slight amount of decomposition. Hydrocinnamaldehyde is obtained by the hydrolysis of the crude acetal, and has also been prepared by von Miller and Rohde (Abstr., 1890, 979); it boils at 104—105° (corr.) under a pressure of 13 mm. The aldehyde undergoes condensation with acetaldehyde in presence of aqueous soda forming *phenopentenal*, CH$_2$Ph·CH$_2$·CH:CH·CHO; this boils at 138—139° (corr.) under a pressure of 13 mm., and shows the ordinary aldehyde reactions. On exposure to the air, it yields an acid melting at 102·5° (corr.), which is probably phenyl-$\alpha\beta$-pentenoic acid. The *phenylhydrazone* crystallises in soft needles melting at about 100°, whilst the *oxime* crystallises in prisms melting at 109° (corr.). Cinnamacetal is converted by alkaline potassium permanganate into *phenylglyceraldehydedimethylacetal*, OH·CHPh·CH(OH)·CH(OMe)$_2$, which crystallises in rhomboidal tablets melting at 79—80° (corr.); this is sparingly soluble in cold water, and does not reduce Fehling's solution even on boiling. The acetal is very readily hydrolysed by very dilute acids, yielding a solution which reduces Fehling's solution in the cold, and contains phenylglyceraldehyde. The *phenylhydrazone*,

OH·CHPh·CH(OH)·CH:N$_2$HPh,

which crystallises out when phenylhydrazine acetate is added to the solution of the aldehyde, forms long, pointed prisms, which melt at 170·5° (corr.). The *sodium hydrogen sulphite* compound crystallises in colourless needles, and is very sparingly soluble in concentrated sodium hydrogen sulphite solution.

When the acetal is hydrolysed with 1 per cent. sulphuric acid, an oil separates which appears to be a polymeride of phenylglyceraldehyde; it solidifies after a time, and then crystallises from alcohol in lustrous leaflets which melt at 114—125°, and could not be obtained pure and of constant composition and melting point; with phenylhydrazine, its alcoholic solution yields the hydrazone described above, and it can be reconverted into the acetal in the usual way. Phenylglyceraldehyde may be regarded as the next lower homologue of phenyltetrose.

A. H.

Acetals Derived from Catechol. By CHARLES MOUREU (*Compt. rend.*, 1898, **126**, 1656—1658).—When catechol is heated in a sealed tube at 175° with monochloracetal and absolute alcohol, *phenoloxyacetal*, OH·C$_6$H$_4$·O·CH$_2$·CH(OEt)$_2$, is formed, together with a certain proportion of *phenylenedioxydiacetal*, C$_6$H$_4$[O·CH$_2$·CH(OEt)$_2$]$_2$. The latter remains undissolved when the product of the reaction is treated with dilute soda, whilst the alkaline solution, on acidification with hydrochloric acid, yields phenoloxyacetal as a heavy, insoluble oil,

which decomposes on distillation, even under diminished pressure. On boiling with dilute sulphuric acid, it is converted into the corresponding *aldehyde*, $OH\cdot C_6H_4\cdot O\cdot CH_2\cdot CHO$, which is a heavy, oily liquid, boiling without decomposition at 139° under a pressure of 9 mm. This substance is soluble in alkalis, and is reprecipitated on the addition of acids to its solutions; it forms a crystalline compound with sodium hydrogen sulphite, and gives the general reactions of aldehydes, but yields no coloration with ferric chloride, although containing phenolic hydroxyl. When heated to 225°, it loses water, and is probably converted into acetylene catechol, which then undergoes polymerisation or oxidation. The *acetate*, $OAc\cdot C_6H_4\cdot O\cdot CH_2\cdot CHO$, boils without decomposition at 141° under a pressure of 8 mm., and decomposes at about 220°. Phenoloxyacetal, when heated to 210—215°, loses a molecule of alcohol, and yields *catechol ethoxyethylenic ether*,

$$C_6H_4{<}\begin{matrix}O\cdot CH_2\\ \quad\ \ |\\ O\cdot CH\cdot OEt\end{matrix}.$$

This is a colourless oil boiling at 247° (corr.) and having a sp. gr. = 1·158 at 0°; on boiling with dilute sulphuric acid, a second molecule of alcohol is eliminated, with formation of the aldehyde previously described.

Phenylenedioxydiacetal is an oily liquid boiling at 195—197° under a pressure of 9 mm., and having a sp. gr. = 1·061 at 0°; by dilute sulphuric acid, it is hydrolysed to the corresponding aldehyde, which is soluble in water, and slightly soluble in ether. N. L.

Derivatives of Vanillin. By ALBERT E. MENKE and WILLIAM B. BENTLEY (*J. Amer. Chem. Soc.*, 1898, **20**, 316—317).—*Chlorovanillin*, obtained by the action of chlorine on vanillin dissolved in chloroform, melts at 166°, and, on reduction with sodium amalgam, gives rise to *chlorovanilloin*, which melts at 255°. A *chloroprotocatechuic acid*, melting at about 235°, appears to be formed when chlorovanillin is fused with potassium hydroxide. On passing chlorine into an alcoholic solution of protocatechuic acid, a resinous substance was formed, from which, by treatment with caustic potash, tetrachlorocatechol was obtained.

The action of dilute nitric acid on vanillin, gives rise to dinitroguaiacol, together with two other *substances*; the first of these is colourless, insoluble in the usual solvents, and melts at about 300°; the second is yellow, melts at 178—179°, is soluble in alcohol, and is either nitrovanillin or an additive compound of this and dinitroguaiacol; with nitric acid, it gives rise to dinitroguaiacol, and on oxidation with potassium permanganate, *nitrovanillic* acid, which melts at 214°, is obtained. W. A. D.

Halogen Derivatives of Phenyl Ethyl Ketone. By A. COLLET (*Compt. rend.*, 1898, **126**, 1577—1579).—The compounds described in this paper were obtained by the action of propionic chloride or α-bromopropionic chloride on chlorobenzene or bromobenzene in presence of aluminium chloride. *Parachlorophenyl ethyl ketone*, which forms small, colourless crystals, melts at about 35—36°, and is soluble in alcohol or carbon bisulphide. When oxidised with alkaline per-

manganate, it yields parachlorobenzoic acid. Its *oxime* forms nacreous lamellæ, which melt at 62—62·5°, whilst the *phenylhydrazone* crystallises in colourless needles which melt at 94—96°. *Parabromophenyl ethyl ketone*, which forms brilliant, colourless needles, melts at 44—45°, and yields parabromobenzoic acid on oxidation. Its *oxime* melts at 90—91°, and its *phenylhydrazone* at 99—101°; both crystallise in needles. *Parachlorophenyl bromethyl ketone* forms brilliant crystals, which melt at 77·5°; it yields parachlorobenzoic acid when oxidised. The *anilide*, $NHPh\cdot CHMe\cdot CO\cdot C_6H_4Cl$, forms yellow needles, which melt at 111—111·5°. Parabromophenyl bromethyl ketone forms brilliant, colourless lamellæ which melt at 84—84·5°; its vapour, and that of the preceding ketone, are very irritating to the eyes. The *anilide* crystallises in yellow scales, which melt at 109·5—110° (compare this vol., i, 139). C. H. B.

Allocinnamic Acid. By CARL LIEBERMANN (*Ber.*, 1898, 31, 2095—2098).—When allocinnamic acid is triturated with fuming sulphuric acid, truxone is produced, together with a small quantity of a bye-product which develops a violet coloration when warmed with potash. This impurity is removed by treatment with chromic acid, and the truxone thus obtained appears to be more soluble in hot glacial acetic acid than that produced from α-truxillic acid (Abstr., 1889, 699), but a mixture of the two gives the same melting point, 294—295°, as either of these preparations. When treated with sulphuric acid, cinnamic acid only yields a trace of truxone. This ready formation of indones lends additional support to the space formula, $\begin{matrix} Ph\cdot C\cdot H \\ \| \\ COOH\cdot C\cdot H \end{matrix}$, for the allocinnamic acid series, and serves to identify these compounds. On treating a mixture of α- and β-dibromocinnamic acids with sulphuric acid, the latter alone is converted into dibromindone, whilst the former remains unaltered.

When Glaser's monobromocinnamic acids are similarly treated, the so-called β-acid (α-bromallocinnamic acid) alone yields an anhydrocompound, to which Leukart gave the formula $C_{17}H_{12}Br_2O_2$, but which may be a monobromotruxone $(C_9H_5BrO)_x$ (Abstr., 1882, 615). The author is unable to corroborate Erlenmeyer's observation (Abstr., 1896, i, 46) that allocinnamic acid, when dissolved in alcohol containing zinc bromide, changes into isocinnamic acid. Solutions of pure allocinnamic acid, after remaining for several months, showed no trace of any change; moreover, allocinnamic acid, its aniline salt, and allocinnamylideneacetic acid were found to have undergone no change after keeping for several years. G. T. M.

Phenyl-γδ-pentenoic Acid. By FRITZ FICHTER and ALEXANDER BAUER (*Ber.*, 1898, 31, 2001—2004. Compare Abstr., 1897, i, 13 and 590).—*Ethylic benzoylglutarate*, $COOEt\cdot CH(COPh)\cdot CH_2\cdot CH_2\cdot COOEt$, synthesised from ethylic sodiobenzoylacetate and ethylic β-iodopropionate, is a colourless liquid boiling at 200—210° under a pressure of 12 mm. On acidic hydrolysis, it gives rise to benzoic and glutaric acids, whilst the ketonic hydrolysis yields γ-benzoylbutyric acid.

δ-Phenyl-δ-valerolactone-γ-carboxylic acid, $COOH\cdot CH{<}{\begin{matrix} CHPh\cdot O \\ CH_2\cdot CH_2 \end{matrix}}{>}CO$,

obtained by reducing the preceding compound with sodium amalgam in dilute alcoholic solution, and subsequently heating the product of reduction in a current of dry air at 125°, crystallises from ether and light petroleum in small, white nodules, and melts at 161°.

Phenyl-γδ-pentenoic acid, $CHPh:CH\cdot CH_2\cdot CH_2\cdot COOH$, produced either by distilling the above lactone, or by boiling its aqueous solution for some hours, crystallises from light petroleum in shining leaflets, melts at 90—91°, and is soluble in ether, carbon bisulphide, chloroform, and hot water. Its melting point and the properties of its salts (the *calcium*, *barium*, and *silver* salts are described) distinguish it from its βγ- and αβ-isomerides (Abstr., 1880, 407, and 1895, i, 223). Like other γδ-unsaturated acids, it is neither reduced by sodium amalgam nor acted on by caustic soda; hydriodic acid reduces it to normal phenylvaleric acid.

γδ-Dibromophenylvaleric acid is obtained by the action of bromine on the γδ-unsaturated acid; it crystallises from light petroleum in colourless needles and melts at 162°. A phenylbromovaleric acid results from the addition of hydrogen bromide to the γδ-acid, which, although having the same melting point as Perrin's γ-bromophenylvaleric acid (Abstr., 1895, i, 224), differs from it in being reconverted into phenyl-γδ-pentenoic acid when boiled with water or digested with sodium carbonate; Perrin's acid, under these conditions, yields phenylvalerolactone.

Benzylideneglutaric acid (Abstr., 1895, i, 141) is produced in small amount by the distillation of δ-phenyl-δ-valerolactonecarboxylic acid in the preparation of phenyl-γδ-pentenoic acid. G. T. M.

Products of the Iodisation of Aromatic Alcohols, Aldehydes, and Acids. By JOHANNES SEIDEL (*J. pr. Chem.*, 1898, [ii], **57**, 495—496. Compare this vol., i, 367).—When moniodanisaldehyde is boiled with alcoholic potash, it yields 3-iodanisic acid, and a moniodanisylic alcohol melting at 84°; the *phenylhydrazone* melts at 106·5—107°, the *oxime* at 129—130°, the *anil* at 107—108°.

3-Iodanisic acid, when heated at 150—160° in the presence of iodine, yields 2:4-di-iodanisoil, melting at 65·5—66·5°. The *methylic* salt of the acid melts at 95°, the *ethylic* salt rather above 65°.

By iodating coumarin, two products are obtained which are very difficult to purify, as they show no tendency to crystallise. Probably they are derivatives of coumaric acid. A *moniodocoumarin* melting at 164—165° and a *di-iodocoumarin* melting at 192° were obtained, however, from the corresponding iodine derivatives of salicylaldehyde by the Perkin reaction. C. F. B.

Condensation of Chloral with Methylic 2:3-Dimethoxybenzoate: Synthesis of Meconine. By PAUL FRITSCH (*Annalen*, 1898, **301**, 352—361. Compare Abstr., 1897, i, 568).—Guaiacolcarboxylic acid separates from water in crystals containing $1H_2O$, and melts at 152°; the *methylic* salt crystallises from methylic alcohol in aggregates of needles and melts at 63°. *Methylic 2:3-dimethoxybenzoate* $C_6H_3(OMe)_2\cdot COOMe$, is deposited from the ethereal solution in lustrous plates, and melts at 47°; it boils at 184—185° under a pressure of 50 mm.

5 : 6-*Dimethoxytrichloromethylphthalide*,

$$C_6H_2(OMe)_2<\begin{matrix}-CO-\\ CH(CCl_3)\end{matrix}>O,$$

obtained by the condensation of methylic 2 : 3-dimethoxybenzoate with chloral under the influence of concentrated sulphuric acid, crystallises from alcohol in stellate aggregates of needles, and melts at 104°.

2-*Carboxy*-3 : 4-*dimethoxymandelic acid*,

$$COOH\cdot C_6H_2(OMe)_2\cdot CH(OH)\cdot COOH,$$

prepared by hydrolysing the foregoing substance with 20 per cent. caustic soda at 50°, separates from water in crystals containing $1H_2O$; it crystallises from wet ethylic acetate in needles containing $2H_2O$, and chars when heated. The *barium* salt crystallises in slender needles containing $4H_2O$. When the acid is heated in small quantities, meconine distils from the charred product. M. O. F.

Action of Phthalic Anhydride on Para- and Meta-hydroxy-diphenylamine. By ARNALDO PIUTTI and R. PICCOLI (*Gazzetta*, 1898, **28**, i, 370—382).—Piutti has previously shown (Abstr., 1884, 448) that phthalic anhydride reacts with secondary monamines yielding disubstituted phthalamic acids or tetra-substituted asymmetric phthalic diamides; the production of the rhodamines by condensing phthalic anhydride with amidophenols is now a commercial process.

On heating phthalic anhydride with parahydroxydiphenylamine, in molecular proportion, at 195°, *parahydroxydiphenylphthalamic acid*, $COOH\cdot C_6H_4\cdot CO\cdot NPh\cdot C_6H_4\cdot OH$, is obtained; it crystallises in colourless prisms melting at 191—192°, and is insoluble in water. The *silver* salt, $C_{20}H_{14}NO_4Ag,3\frac{1}{2}H_2O$, and the *copper* salt,

$$(C_{20}H_{14}NO_4)_2Cu,4H_2O,$$

were prepared; the *ethylic* salt, $C_{20}H_{14}NO_4Et$, crystallises in needles melting at 166—168°. The *methoxy*-derivative, $C_{21}H_{17}NO_4$, prepared by the aid of methylic iodide and potash, is amorphous and melts at 90—92°. *Parethoxydiphenylphthalamic acid*, $C_{22}H_{19}NO_4$, is also amorphous and melts at 80—82°; the *silver* salts of both these acids were analysed. The benzoyl and acetyl derivatives of the hydroxy-acid melt below 100°, but are not well-defined.

No well-defined new compound could be isolated from the product of the reaction of two molecular proportions of the amine with one of anhydride.

Metahydroxydiphenylamine and phthalic anhydride react in molecular proportion with production of *metahydroxydiphenylphthalamic acid*, $C_{20}H_{15}NO_4$, which forms white, crystalline crusts melting at 191—192°; it readily yields rhodamines when heated with dehydrating agents, and its *silver* salt is anhydrous and crystalline. The *ethylic* salt forms crystalline crusts melting at 155—157°. The *methoxy*-derivative of the acid, $C_{21}H_{17}NO_4$, is very soluble in organic solvents and melts at 95—98° the corresponding *ethoxy*-derivative is similar and melts at 88—90°. The *silver* salts of both acids were analysed, but the benzoyl and acetyl derivatives of the hydroxy-acid are, again, not characteristic.

On heating metahydroxydiphenylamine (2 mols.) with phthalic anhydride (1 mol.) at 160°, the diphenylrhodamine,

$$COOH\cdot C_6H_4\cdot C{<}^{C_6H_3(NHPh)}_{C_6H_3(=NPh)}{>}O,$$

melting at 260—262° is obtained; its solutions in benzene and carbon bisulphide are colourless. W. J. P.

Propylphthalide and its Hydrolysis by Caustic Alkalis. By PIETRO GUCCI (*Gazzetta*, 1898, **28**, i, 297—304).—On heating a mixture of phthalic anhydride, zinc dust, and normal propylic iodide, much gas is evolved, and the residue, when distilled in a current of steam, yields *propylphthalide*, $C_6H_4{<}^{CHPr}_{CO}{>}O$, as an oil which boils at 243—247° under 220 mm. pressure and at 293—297° under 735 mm. pressure. When heated, it yields propylene and phthalide, and when fused with soda gives benzoic acid and butyraldehyde. Its odour resembles that of sedanolide, a tetrahydrobutylphthalide extracted from oil of celery by Ciamician and Silber. The monalkyl phthalides possess an odour of celery which is independent of the degree of hydrogenation of the aromatic nucleus. W. J. P.

New Method of Preparing Ethylic Orcintricarboxylate [Dihydroxydicarboxyphenylacetate]. By HANS VON PECHMANN and LUDWIG WOLMAN (*Ber.*, 1898, **31**, 2014—2017. Compare Abstr., 1886, 802).—If in the preparation of ethylic acetonedicarboxylate the alcoholic solution of ethylic acetonedicarboxylic acid saturated with hydrogen chloride is allowed to remain for 2 or 3 weeks, a considerable yield of ethylic orcintricarboxylate (dihydroxydicarboxyphenylacetate) is obtained.

The diethylic salt, $(COOEt)_2C_6H(OH)_2\cdot CH_2\cdot COOH$, produced from the preceding compound on hydrolysis with dilute alkali in the cold, crystallises from alcohol in rhombohedra, melts at 183—184°, and is soluble in alcohol, acetone, chloroform, and hot water. It gives the homofluorescein reaction with chloroform and caustic soda, and is coloured red by ferric chloride.

Dihydroxyphenylacetic acid is obtained by the hydrolysis of the preceding compound with the aid of heat, and is isolated by means of its *lead* salt, $(C_8H_7O_4)_2Pb + 2H_2O$; when obtained by evaporating its aqueous solution to dryness, the acid melts at 127—128°, but if allowed to crystallise spontaneously, its melting point is 54°; doubtless this is due to difference in the amount of water of crystallisation in the two cases.

Ethylic dihydroxydicarboxyphenylacetamide,

$$(COOEt)_2C_6H(OH)_2\cdot CH_2\cdot CO\cdot NH_2,$$

obtained on treating an alcoholic solution of ethylic orcintricarboxylate with concentrated ammonia, crystallises from alcohol in slender needles, and melts at 186°; it is sparingly soluble in the ordinary solvents, dissolving most readily in chloroform and acetone. Its *monosodium* salt crystallises from alcohol in prisms, and is decomposed by water.

Dihydroxydicarboxyphenylacetamide, produced from the above amide by digestion with cold caustic soda, crystallises from alcohol in prisms and melts at 221—222°. G. T. M.

Derivatives of Benzenesulphonic Acid. By THOMAS H. NORTON (*J. Amer. Chem. Soc.*, 1897, **19**, 835—838).—Benzenesulphonic bromide can readily be prepared by treating sodium benzenesulphonate with phosphorus pentabromide, about one-fourth of the theoretical yield being obtained. *Sodium benzenesulphonate* crystallises in small, white leaflets, and melts at about 450°; the *potassium* salt forms long, colourless needles and melts at about 408°, whilst the *ammonium* salt is deliquescent, and melts and decomposes at 256°; the *lithium* salt crystallises in stellate groups of white needles and melts at a dull red heat. A. H.

Hydroxysulphonic Acids and Sultones. By WILHELM MARCKWALD and H. H. FRAHNE (*Ber.*, 1898, **31**, 1854—1865).—Orthonitrobenzylic chloride was converted into *orthonitrobenzylsulphonic acid*, $NO_2\cdot C_6H_4\cdot CH_2\cdot SO_3H$, by boiling it with a saturated aqueous solution of sodium sulphite; this acid forms hygroscopic crystals; the *sodium*, *barium*, and *silver* salts crystallise with 1, 3 (of which only 2 are lost at 100°), and $1H_2O$, respectively. When reduced with iron and acetic acid, the acid is converted into *orthamidobenzylsulphonic acid*, $NH_2\cdot C_6H_4\cdot CH_2\cdot SO_3H$, a crystalline substance, the *sodium* salt of which crystallises with $1H_2O$. When this salt and sodium nitrite are dissolved in water, and dilute sulphuric acid added to the well cooled mixture, which is then warmed on the water bath, *benzylsultone*, $C_6H_4{<}{\scriptstyle\genfrac{}{}{0pt}{}{CH_2}{O}}{>}SO_2$, is formed. This melts at 86°, and is not affected by alkalis in the cold, but when boiled with them, it yields salts of *orthohydroxybenzylsulphonic acid*, $OH\cdot C_6H_4\cdot CH_2\cdot SO_3H$, itself a syrupy liquid; the *barium* salt crystallises with $4H_2O$, the *lead* salt with $7H_2O$; the *ammonium* salt is anhydrous; from the acid, the sultone is not easily regenerated, but the transformation can be effected by the action of phosphorus pentachloride. The sultone, on warming with bromine in chloroform solution, yields *monobromobenzylsultone* [$CH_2 : O : Br = 1 : 2 : 5$, probably], which melts at 147°; with fuming nitric acid and sulphuric acid, it yields *mononitrobenzylsultone*, melting at 148°, and this is converted into *nitrohydroxybenzylsulphonic acid*, $OH\cdot C_6H_3(NO_2)\cdot CH_2\cdot SO_3H$, when it is boiled with water for a long time; this acid forms hygroscopic crystals, and yields a *mono-* and a *di-potassium* salt, the latter crystallising with $1H_2O$, whilst with ammonia it forms, not the ammonium salt, but *nitro-orthohydroxybenzylsulphonamide*, $OH\cdot C_6H_3(NO_2)\cdot CH_2\cdot SO_2\cdot NH_2$; this amide melts and decomposes at 199°, and has pronounced acid properties; its *potassium* and *silver* derivatives were prepared, and from the latter and methylic iodide, *nitro-orthomethoxybenzylsulphonamide*, melting at about 100°, was obtained. Nitrobenzylsultone can be reduced with tin and hydrochloric acid to *amidobenzylsultone*, $NH_2\cdot C_6H_3{<}{\scriptstyle\genfrac{}{}{0pt}{}{CH_2}{O}}{>}SO_2$, which melts at 138°; the *hydrochloride*, and the yellow *picrate*, the latter melting and decomposing at about 170°, were prepared; the base, when diazotised, forms *orthohydroxydiazobenzylsulphonic acid*, $OH\cdot C_6H_3{<}{\scriptstyle\genfrac{}{}{0pt}{}{CH_2\cdot SO_2}{N:N\cdot O}}$, which was obtained impure as a syrup.

γ-Hydroxypropanesulphonic acid, $OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot SO_3H$, can be obtained quite readily by boiling allylic alcohol with a strong solution of potassium hydrogen sulphite, and also by reducing acraldehydesulphonic acid, $CHO\cdot CH_2\cdot CH_2\cdot SO_3H$ (Rosenthal, Abstr., 1886, 866), with potassium amalgam. It cannot be made to yield a sultone.

C. F. B.

Synthesis of Safranine. By GEORGE F. JAUBERT (*Compt. rend.*, 1898, **126**, 1515—1518).—*Trinitrophenosafranine* is obtained by oxidising a mixture of trinitrophenylmetaphenylenediamine with paraphenylenediamine, in molecular proportion, in acetic acid solution, and boiling the alcoholic solution of the indamine thus obtained; it has considerable tinctorial power, and dyes ruby-red on cotton mordanted with tannin or tartar emetic. The trinitrophenylmetaphenylenediamine, prepared by the action of picryl chloride on metaphenylenediamine hydrochloride in presence of alcohol and dry sodium acetate, crystallises from acetone in orange prisms, melts at 207°, and is only slightly soluble in alcohol or acetic acid, but readily in solutions of alkali hydroxides.

Trinitrodimethylphenosafranine is obtained by the action of nitrosodimethylaniline on trinitrophenylmetaphenylenediamine, or by the oxidation of a mixture of paraphenylenediamine and trinitrophenyldimethylmetaphenylenediamine, in molecular proportion, the indamine thus obtained being boiled with alcohol. It forms green needles, and dyes a very fast red-violet on cotton mordanted with tannin or with tartar emetic. Trinitrophenyldimethylmetaphenylenediamine can be obtained by the action of picryl chloride on metamidodimethylaniline hydrochloride in presence of alcohol and dry sodium acetate; it forms red crystals.

Since, in these cases, there is double substitution in the ortho-position relatively to the nitrogen in the phenylic group, the formation of the safranines would be impossible if their constitution were represented by Nietzki's asymmetrical formula, and the author regards the formation of the compounds described in this paper as additional proof of the validity of his symmetrical formula for safranines (this vol., i, 494).

C. H. B.

Dibenzylidenediethyl Ketone. By DANIEL VORLÄNDER and F. WILCKE (*Ber.*, 1898, **31**, 1886—1888).—When the compound $CO{<}{\substack{CHMe\cdot CHPh\\ CHMe\cdot CHPh}}{>}O$ (Abstr., 1896, i, 546, 603) is dissolved in acetic acid, dry hydrogen chloride gas passed into the boiling solution for 2 hours, and then into the cooled solution to saturation, the solution being finally allowed to remain for 4 days, *dibenzylidenediethyl ketone*, $CO(CMe{:}CHPh)_2$, is precipitated when the product is poured into water. This ketone melts at 122°, is not decomposed by boiling hydrochloric acid, unites with bromine in chloroform solution, although but slowly, to form a *tetrabromide*, which decomposes and melts at about 180°, and forms an *oxime* which melts at 157—159°.

C. F. B.

Oxylactones—Ketolactones. By EMIL ERLENMEYER, jun., and MICHAEL LUX (*Ber.*, 1898, **31**, 2218—2224. Compare Erlenmeyer and Knight, Abstr., 1894, i, 592).—The *benzyl* derivative of α-oxy-

β-phenyl-γ-benzylbutyrolactone is obtained when the lactone (10 grams) and sodium (0·88 gram) are separately dissolved in alsolute alcohol and then mixed and boiled with benzylic chloride for 6 hours, or until the solution is neutral. When recrystallised from alcohol, it forms large prisms melting at 67°, sparingly soluble in water, but readily in the usual organic solvents. The *benzoyl* derivative, $C_{24}H_{18}O_4$, readily obtained by the Schotten-Baumann method, crystallises from alcohol in colourless plates melting at 137°, and gives no coloration with ferric chloride.

A better yield of α-oxy-$\beta\gamma$-diphenylbutyrolactone (Abstr., 1894, i, 592) is obtained by suspending ethylic phenylcyanopyruvic acid in concentrated hydrochloric acid, mixing with the requisite quantity of benzaldehyde, and allowing the mixture to remain at the ordinary temperature for 14 days, with occasional shaking; from 10 grams of the ethylic salt, 10 grams of the lactone may be obtained. The *benzoyl* derivative, $C_{23}H_{16}O_4$, crystallises from its alcoholic solution in needles melting at 137°; it is insoluble in water, and is not coloured by ferric chloride.

When the lactone is distilled, a copious evolution of gas occurs, and stilbene is formed, a reaction which is completely in accordance with the constitution of the lactone previously given, namely, $\begin{matrix}\text{CHPh·CO}\\ \vert \\ \text{CHPh—O}\end{matrix}\!\!>\!\text{CO}$.

J. J. S.

Conversion of an $\alpha\gamma$-Dihydroxy-acid into the Corresponding Ketone. By EMIL ERLENMEYER, jun., and MICHAEL LUX (*Ber.*, 1898, 31, 2224—2238).—When α-oxy-$\beta\gamma$-diphenylbutyrolactone (compare preceding abstract) is suspended in water, reduced with 4 per cent. sodium amalgam, and the solution neutralised from time to time with hydrochloric acid, a mixture of two *stereoisomeric hydroxylactones*, $\text{CHPh}\!<\!\begin{matrix}\text{CHPh—O}\\ \text{CH(OH)·CO}\end{matrix}$, is obtained. The mixture, which is at first syrupy, may be purified by dissolving it in chloroform and adding light petroleum, when colourless needles melting at 127° separate. The hydrochloric acid solution also yields the same two compounds, namely, the one melting at 127° and a second at 170°. Both compounds are sparingly soluble in water, ether, or light petroleum, but dissolve readily in warm alcohol, benzene, or chloroform. Phenyl-α-lactic acid may also be isolated from the products of reduction; it is probably formed by the decomposition of the oxylactone into phenylpyruvic acid and benzaldehyde, and the subsequent reduction of the phenylpyruvic acid.

They are both readily hydrolysed to the *corresponding dihydroxy-acids* by sodium hydroxide, and as the sodium salt derived from the lactone melting at 127° is much more sparingly soluble than the isomeric salt, this affords a convenient method of separating the two compounds. The *silver* salts of the two hydroxy-acids have been prepared and analysed. When the reduction of the oxylactone is brought about by the aid of zinc dust and acetic acid, the products are desylacetic acid, diphenylcrotonolactone, previously obtained by Klingemann (Abstr., 1892, 1002) by heating desylacetic acid, and finally an

acid, $C_{16}H_{14}O_3$, isomeric with desylacetic acid and with the two hydroxylactones. This acid is found as its zinc salt mixed with the zinc which has not been acted on and the zinc acetate; it is sparingly soluble in cold water or light petroleum, but dissolves readily in the usual organic solvents, and its alcoholic solution gives no coloration with ferric chloride. Its *methylic* salt, $C_{15}H_{13}O\cdot COOMe$, crystallises from hot light petroleum in glistening needles melting at 89°; it is readily soluble in ether, alcohol, benzene, chloroform or carbon bisulphide, but is only sparingly soluble in water or light petroleum. The acid combines with bromine, yielding a solid product from which two compounds may be obtained by crystallisation from a mixture of chloroform and light petroleum; the one crystallises in quadratic plates decomposing at 140—144° and the other in colourless needles turning brown at 90° and decomposing at 105°.

When the acid, $C_{16}H_{14}O_3$, is heated with dilute acetic or hydrochloric acid, it is converted into diphenylcrotonolactone, and this in its turn into desylacetic acid. The two hydroxylactones (melting at 127° and 170° respectively) behave with acetic or hydrochloric acid in an exactly similar manner. The conversion of the hydroxylactone into the unsaturated lactone seems to be brought about as follows.

$$CHPh<\begin{matrix}CHPh\text{—}O\\ CH(OH)\cdot CO\end{matrix} \rightarrow CHPh<\begin{matrix}CPh\cdot O\\ CH\text{—}CO\end{matrix} \rightarrow CPh\leqslant\begin{matrix}CPh\cdot O\\ CH_2\cdot CO\end{matrix}$$

the last stage of which is compared with the conversion of

$$O<\begin{matrix}CHPh\\ CH_2\end{matrix} \text{ into } O{:}CH\cdot CH_2Ph.$$

For the acid $C_{16}H_{14}O_3$, the constitution $\begin{matrix}OH\cdot CPh\text{—}\\ CHPh\end{matrix}>CH\cdot COOH$ is suggested, the conversion of this acid into diphenylcrotonolactone and desylacetic acid being represented as follows.

$$\begin{matrix}OH\cdot CPh\text{—}\\ CHPh\end{matrix}>CH\cdot COOH \rightarrow OH\cdot CPh{:}CPh\cdot CH_2\cdot COOH$$

$$\swarrow \qquad \searrow$$

$$\begin{matrix}CH_2\text{—}CO\\ CPh{:}CPh\end{matrix}>O \qquad COPh\cdot CHPh\cdot CH_2\cdot COOH.$$

J. J. S.

Remarkable Conversion of an α-Ketonic Acid into the Corresponding α-Amido-acid. By EMIL ERLENMEYER, jun. (*Ber.*, 1898, 31, 2238—2240).—By the condensation of phenaceturic acid with benzaldehyde, a compound, $\begin{matrix}CHPh{:}C\\ CH_2Ph\cdot CO\cdot N\end{matrix}>CO$, is obtained; it is a pale yellow substance with neutral properties, and when warmed with sodium hydroxide yields an acid,

$$CHPh{:}C(COOH)\cdot NH\cdot CO\cdot CH_2Ph,$$

which crystallises well and yields a somewhat sparingly soluble sodium salt. When dissolved in sodium carbonate and reduced with 4 per cent. sodium amalgam while a current of carbonic anhydride is passed through the liquid, this acid yields another acid, $C_{17}H_{17}NO_3$, melting at 126° and identical with that obtained from phenylpyruvic acid

(this vol., i, 197), so that the constitution previously given is established. J. J. S.

Dialkylamido-orthobenzoylbenzoic and Dialkylamido-orthobenzylbenzoic Acids. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1898, **126**, 1248—1251).—The crystals of dimethylamido-orthobenzoylbenzoic acid which melt at 199°, are hydrated, and effloresce readily; they become anhydrous at 120°, and then melt at 203—204° (uncorr.). The acid also crystallises with methylic alcohol, but forms no similar compound with propylic and butylic alcohols. The magnesium salt, with $6H_2O$, crystallises in large, pale yellow crystals; the barium salt, with $2H_2O$, in pale yellow, prismatic needles; the platinochloride, with $2H_2O$, in transparent, orange prisms. When the barium salt is heated, it yields a dimethylparamidobenzophenone, melting at 92° and identical with Doebner's benzodimethylaniline.

The phenylhydrazine compound of the acid, which is derived from equal molecular proportions of its two components, forms colourless needles melting at 158°. From benzene, it crystallises in large, brilliant prisms which contain benzene and effloresce rapidly.

When the acid is suspended in water and treated with sodium amalgam, it yields dimethylamidomonophenylphthalide, which crystallises from chloroform in nacreous leaflets melting at 188°. It has been obtained by Ebert (Abstr., 1896, i, 441), and by Limpricht.

Dimethylamidobenzylbenzoic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe_2$, obtained by the prolonged action of sodium amalgam, or, better, by the action of zinc powder and potassium hydroxide, melts at 174°, and crystallises from acetic acid or alcohol in large prisms or leaflets. Its *methylic* salt crystallises in large, colourless, transparent prisms, which melt at 62°, and can be distilled without decomposing. When dissolved in acetic acid and mixed with lead peroxide, it gives an intense violet coloration.

Diethylamidobenzoylbenzoic acid crystallises from methylic or ethylic alcohol in large prisms containing one molecular proportion of the alcohol; the anhydrous acid melts at 180°. When heated with diethylaniline in presence of acetic anhydride or phosphorus trichloride, it yields diethylanilinephthalein, which crystallises in leaflets or needles melting at 128°. With sodium amalgam, the acid yields a phthalide, and with zinc powder and sodium hydroxide, it yields diethylamidobenzylbenzoic acid melting at 108°.

Diethylamidometahydroxyorthobenzoylbenzoic acid,

$$COOH\cdot C_6H_4\cdot CO\cdot C_6H_3(OH)\cdot NEt_2,$$

forms slender, white needles, which melt and decompose at 203°; it is obtained by the condensation of phthalic anhydride and diethylamidoresorcinol, in molecular proportion. When reduced with zinc powder and potassium hydroxide solution, it yields *diethylamidometahydroxybenzylbenzoic acid*, which will be described later. C. H. B.

Phenoxycinnamic [Hydroxyphenylcinnamic] Acid. By ALB. J. J. VAN DE VELDE (*Rec. Trav. Chim.*, 1897, **16**, 287—288, from *Bull. Acad. Roy. Belg.*, 1897, [iii], **33**, 221—229).—*Hydroxyphenylcinnamic acid*, $CHPh\colon C(C_6H_4\cdot OH)\cdot COOH$, is readily obtained when benzaldehyde, sodium hydroxyphenylacetate, and acetic anhydride

are heated at 140—160° during 18 hours; it is best extracted by large quantities of boiling water, and crystallises as the solution cools. It melts at 121°, and dissolves readily in alcohol, ether, benzene, or chloroform. Its *alkali* salts are soluble in both alcohol and water; its *barium, calcium, lead* and *silver* salts are insoluble; its *aniline* salt melts at 136°, and dissolves readily in organic solvents; its *phenylic* salt melts at 74°.

When reduced with sodium amalgam and water, it yields *hydroxydiphenylpropionic acid*, $CH_2Ph\cdot CH(C_6H_4\cdot OH)\cdot COOH$, melting at 81°.

J. J. S.

Notes. By SIEGMUND GABRIEL and GEORG ESCHENBACH (*Ber.*, 1898, **31**, 1578—1583).—Sodium ethylenebenzhydrylcarboxylate,

$$C_2H_4[CH(OH)\cdot C_6H_4\cdot COONa]_2,$$

was found some time ago (Abstr., 1878, 428) not to lose water at 200°, although the formation of a substance, $C_2H_2(CH\cdot C_6H_4\cdot COONa)_2$, was expected; it has now been ascertained that, although it loses no water at 212°, at 310° it does lose 1 mol., and yields a product which melts at 208—210°, and appears to be *tetrahydrofurandibenzoic acid*, $C_2H_4{<}{CH(C_6H_4\cdot COOH) \atop CH(C_6H_4\cdot COOH)}{>}O$; the *barium*, with $3H_2O$, and *silver* salts of this acid were prepared and analysed.

Phenylethylenediamine, $NH_2\cdot CH_2\cdot CH_2\cdot NHPh$ (Abstr., 1889, 1166), reacts with benzoin, when the two substances are heated together for three-quarters of an hour at 145—150°, in the same way as orthamidoditolylamine, $NH_2\cdot C_6H_3Me\cdot NH\cdot C_6H_4Me$, does (O. Fischer, Abstr., 1891, 748); the product is 1 : 2 : 3-*triphenyltetrahydropyrazine*, $N{<}{CH_2—CH_2 \atop CPh\cdot CHPh}{>}NPh$, isomeric with that obtained by Garzino (Abstr., 1893, i, 428); it begins to melt at about 110°; its *hydrochloride*, with $2HCl + H_2O$, melts at 224°.

When orthocyanobenzylic cyanide is heated with benzaldehyde and a little piperidine for half an hour at 150°, *ortho-α-dicyanostilbene*, $CN\cdot C_6H_4\cdot C(CN){:}CHPh$, is formed; it melts at 125·5°.

C. F. B.

Diketohydrindenecarboxylic Acid. By FRITZ EPHRAIM (*Ber.*, 1898, **31**, 2084—2090).—*Ethylic hemimellithenetricarboxylate*, prepared by treating the silver salt of hemimellithenetricarboxylic acid with ethylic iodide, crystallises from alcohol and ether, and melts at 39°. When ethylic acetate is added to a mixture of this substance and sodium, heated on the water bath, the *sodium* derivative of *diethylic diketohydrindenedicarboxylate* is synthesised; the solution obtained by extracting the mixture with hot water deposits this substance in yellow crystals which contain $1H_2O$. The sodium derivative is decomposed by acids, yielding the free diethylic salt,

$$COOEt\cdot C_6H_3{<}{CO \atop CO}{>}CH\cdot COOEt,$$

which is precipitated in yellow needles also containing $1H_2O$.

The *sodium* derivative of *sodium ethylic diketohydrindenedicarboxylate*, $COONa\cdot C_6H_3{<}{CO \atop CO}{>}CNa\cdot COOEt$, is also formed in the above reaction, and is obtained from the aqueous extract, after filtering off the above

mentioned yellow crystals, by saturating it with carbonic anhydride, evaporating to dryness, and extracting the residue with hot alcohol; from this solution, it separates as a pale yellow, crystalline powder. The free acid is unstable.

Both the sodium derivatives, when boiled with acids, lose the carboxyl group attached to the indene ring, by the elimination of carbonic anhydride, but the diketohydrindenecarboxylic acid, $COOH\cdot C_6H_4<\substack{CO \\ CO}>CH_2$, and its ethylic salt which should be formed, cannot be isolated owing to the readiness with which they undergo further condensation. The *dioxime* of the latter compound was, however, obtained, $COOEt\cdot C_6H_4<\substack{C(:NOH) \\ C(:NOH)}>CH_2$; it crystallises from dilute alcohol in white needles and melts at 186°.

Anhydrobisdiketohydrindenecarboxylic acid,

$$COOH\cdot C_6H_3<\substack{CO \\ CO}>C:C<\substack{CH_2 \\ C_6H_3(COOH)}>CO,$$

results from the condensation of diketohydrindenecarboxylic acid in the presence of hydrochloric acid, and can be obtained in dark green flakes; its alkali salts have a reddish-violet colour, and the lead and silver salts form violet precipitates; it is somewhat soluble in water, and dyes unmordanted wool.

Dianhydrobisdiketohydrindenecarboxylic acid, $C_{20}H_8O_6$, obtained by boiling sodium ethylic diketohydrindenecarboxylate with sulphuric acid, is precipitated in green flakes; analysis of its *silver* salt indicates that it is a dibasic acid.

Wislicenus and Reitzenstein noticed that anhydrobisdiketohydrindene underwent further condensation, and that two substances were produced, a red compound which was identified as dianhydrobisdiketohydrindene, and a yellow product which was not obtained pure, and, on further treatment with sulphuric acid, changed into the red compound. The author finds, on the contrary, that the red compound, when suspended in boiling alcohol, is quantitatively converted into the yellow substance which has the same composition, $C_{36}H_{16}O_4$. On heating with aniline, the red dianhydrobisdiketohydrindene readily yields an *anilido*-compound, $C_{42}H_{21}O_3N$, whereas the yellow substance remains unaltered. G. T. M.

Dimethoxydiketohydrindene and its Derivatives. By JOSEF LANDAU (*Ber.*, 1898, **31**, 2090—2094).—Ethylic hemipinate is best prepared by the action of ethylic iodide on the silver salt of hemipinic acid.

The *sodium* derivative of *ethylic dimethoxydiketohydrindenecarboxylate*, $C_6H_3(OMe)_2<\substack{CO \\ CO}>CNa\cdot COOEt$, is produced by heating ethylic hemipinate with ethylic acetate and caustic soda at 100°; the product of reaction, after washing with ether, is dissolved in water, the solution saturated with carbonic anhydride, evaporated to dryness, and the residue extracted in a Soxhlet apparatus with absolute alcohol. The compound separates as a yellow, crystalline powder. On adding acid to a solution of this substance, the *ethylic dimethoxydiketohydrindenecarboxylate*, is obtained in well-defined yellow needles, which decom-

pose at 58° ; it is easily soluble in ether, alcohol, benzene, and acetone, less so in cold water and petroleum; caustic soda regenerates the sodium derivative.

Dimethoxydiketohydrindene, $C_6H_2(OMe)_2{<}{\scriptstyle CO \atop \scriptstyle CO}{>}CH_2$, is produced on boiling the preceding compound, or even on digesting it with moist ether; it crystallises from ether or light petroleum in needles having a silvery lustre, melts at 113—115°, and is soluble in the usual solvents; dilute soda dissolves it, forming a sodium derivative.

Anhydrobisdimethoxydiketohydrindene,

$$C_6H_2(OMe)_2{<}{\scriptstyle CO \atop \scriptstyle CO}{>}C{=}C{<}{\scriptstyle CH_2 \atop \scriptstyle C_6H_2(OMe_2)}{>}CO,$$

is obtained either on heating the preceding compound for some time above its melting point, or on boiling its solution in dilute acids; it crystallises from 50 per cent. acetic acid in yellow, microscopic needles, melts at 205°, dissolves in alkalis forming a red solution, gives a violet coloration with concentrated sulphuric acid, and does not dye with mordants. By heating this substance with fuming hydrochloric acid at 130°, the methyl groups are eliminated, a dark green substance being formed which has not yet been obtained pure, but is probably either tetrahydroxyanhydrobisdiketohydrindene or an anhydride of this substance; it produces coloured lakes with mordants, those with the oxides of iron and aluminium being brown; in this respect, the compound resembles anthragallol, rufigallic acid, and the substance obtained by Kostanecki from diketohydrindene and protocatechuic aldehyde (Abstr., 1897, i, 425). G. T. M.

Metallic Derivatives of Dinitro-α-naphthol. By THOMAS H. NORTON and H. LOEWENSTEIN (*J. Amer. Chem. Soc.*, 1897, **19**, 923—927).—A study of these compounds indicates that the metal is without influence on the tinctorial properties of the colouring matter.

Lithium dinitro-α-naphthoxide, $C_{10}H_5(NO_2)_2\cdot OLi$, produced by boiling an excess of dinitro-α-naphthol with an aqueous solution of lithium carbonate, separates as a crimson powder soluble in water, alcohol, and ether, but insoluble in carbon bisulphide and benzene.

Magnesium dinitro-α-naphthoxide, $[C_{10}H_5(NO_2)_2\cdot O]_2Mg$, forms rosettes of red needles soluble in water, alcohol, and ether.

Zinc dinitro-α-naphthoxide, $[C_{10}H_5(NO_2)_2\cdot O]_2Zn$, crystallises either in reddish-yellow needles, or in reddish, rhomboidal plates.

Copper dinitro-α-naphthoxide, $[C_{10}H_5(NO_2)_2\cdot O]_2Cu$, is a dark brown powder, and the most insoluble salt of the series. All these salts are anhydrous, and explode when heated. G. T. M.

Amido-derivatives of Dinitro-α-naphthol, and its Chlorination. By THOMAS H. NORTON and IRWIN J. SMITH (*J. Amer. Chem. Soc.*, 1897, **19**, 927—930).—*Trimethylamine-dinitro-α-naphthol*,

$$OH\cdot C_{10}H_5(NO_2)_2,NMe_3,$$

prepared by boiling dinitro-α-naphthol with an aqueous solution of trimethylamine, crystallises from alcohol in lustrous, red needles melting at 190°; it is soluble in water, alcohol, and ether, and insoluble in carbon bisulphide and benzene.

Aniline-dinitro-α-naphthol, $OH \cdot C_{10}H_5(NO_2)_2,NH_2 \cdot C_6H_5$, prepared by heating together alcoholic solutions of dinitro-α-naphthol and aniline, crystallises in yellow needles melting at 129°; it is soluble in hot water, alcohol, and ether, and sparingly so in carbon bisulphide and benzene.

Orthotoluidine-dinitro-α-naphthol, $OH \cdot C_{10}H_5(NO_2)_2,NH_2 \cdot C_7H_7$, crystallises in yellow, silky needles melting at 132°; it is more soluble than the preceding salt.

Dimethylaniline-dinitro-α-naphthol, $OH \cdot C_{10}H_5(NO_2)_2,NMe_2 \cdot C_6H_5$, melts at 115°, and is soluble in water, alcohol, and ether, but insoluble in benzene.

Chlorination of dinitro-α-naphthol yields a dark yellow, viscous mass having no definite melting point; it is free from nitrogen and contains 13·7 per cent. of chlorine. G. T. M.

Synthesis of Phenanthrene and Hydrated Phenanthrene Derivatives from 1-Naphthoic Acid. By PAUL RABE (*Ber.*, 1898, 31, 1896—1902).—1-Naphthoic acid, obtained by heating 1-naphthonitrile with a mixture of sulphuric and acetic acids, was converted into Δ_1-dihydro-1-naphthoic acid by reduction with sodium amalgam in warm alkaline solution, and from the acid, *ethylic* Δ_1*-dihydro-1-naphthoate*, boiling at 305—306° under 748 mm. pressure, was prepared; by heating this for 48 hours with alcoholic sodium ethoxide and ethylic acetoacetate, and acidifying the product with dilute sulphuric acid, an oil was obtained which consisted largely of ethylic diketo-octohydrophenanthrenecarboxylate,

$$CH_2 <\begin{matrix} C_6H_4 \cdot CH \cdot CO \cdot CH_2 \text{———} \\ CH_2 \cdot CH \cdot CH(COOEt) \end{matrix}> CO,$$

for after hydrolysis with alcoholic potash, it yields an oily acid which, when heated on the water bath, loses carbonic anhydride and forms *diketo-octohydrophenanthrene*. This melts and decomposes at about 160°, and when distilled with zinc dust yields an oil which presumably is crude phenanthrene, for it can be oxidised to phenanthraquinone; the diketo-octohydrophenanthrene functions as a monobasic acid (the *barium* salt was analysed), so that one of the ketonic oxygens is capable of transformation into enolic hydroxyl; with diazobenzene chloride, it yields an orange *phenylhydrazone* which melts at 156°.

C. F. B.

Oil of Savin (Oleum Sabinæ). By EMIL FROMM (*Ber.*, 1898, 31, 2025—2031).—When fractionally distilled, oil of savin yields three fractions: the first comes over below 195°, and consists mainly of terpenes, which, on further fractionation, distil between 156° and 170°; the second fraction distils between 195° and 235°, and consists mainly of ethereal salts; the third fraction passes over between 235° and 310°, and consists mainly of resins together with cadinene (Wallach, Abstr., 1887, 596). The second fraction, when further fractionated, yields an oil passing over between 222° and 224°, and consisting of the acetate of an alcohol, $C_{10}H_{15} \cdot OH$, which the author terms *sabinol*. Schimmel and Co. have previously stated that the oil contains the acetate of an alcohol, $C_{10}H_{18}O$. Sabinol is formed when the acetate (b. p. 222—224°) is hydrolysed with alcoholic potash, but is more readily obtained by

boiling the crude oil for half an hour with alcoholic potash, and then distilling in a current of steam; the oil which passes over is rectified, and by repeated fractionation the alcohol is obtained as a colourless oil, with a faint odour, and boiling at 208—209°. The yield is about 50 per cent. of the crude oil. Sabinol absorbs bromine, iodine, and hydrogen chloride, but crystalline products cannot be obtained. When treated with strong dehydrating agents, a small quantity of an oil, boiling at 175°, is obtained, together with a considerable quantity of resin.

When the alcohol is oxidised in the cold with a neutral saturated solution of potassium permanganate as long as the latter becomes decolorised, a quantitative yield of α-tanacetogendicarboxylic acid, $C_9H_{14}O_4$, is obtained. This acid, when heated to about 240°, loses carbonic anhydride and yields a monobasic *acid*, $C_8H_{14}O_2$; this can best be purified by dissolving it in sodium carbonate solution, and subsequently distilling, when it passes over at 229°. J. J. S.

Orientation in the Terpene Series: Conversion of Monocyclic Terpenes into the Corresponding Derivatives of Benzene. II. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1898, 31, 2067—2079. Compare this vol., i, 442).—When sylvestrene dihydrobromide is brominated and then reduced with zinc dust and hydrochloric acid, or sodium and alcohol, a hydrocarbon is obtained which, when freed from unsaturated compounds by the aid of potassium permanganate, is identical with metacymene.

The authors suggest the prefix *gem* (from "gem" twin) for compounds containing two alkyl groups attached to the same carbon atom; for example, unsymmetrical dimethylsuccinic acid is termed *gem*-dimethylsuccinic acid.

Eucarvone is obtained from carvone in the same manner as carone from dihydrocarvone, it is therefore probable that eucarvone differs from carone merely by a double linking, although the two compounds behave quite differently when oxidised. It has already been shown that carone, on oxidation, yields caronic acid or *gem*-dimethyltrimethylenedicarboxylic acid (Perkin and Thorpe, Proc., 1898, 107), whereas dihydroeucarvone or methyl-*gem*-dimethylcycloheptenone, when oxidised with a saturated solution of potassium permanganate, yields *gem*-dimethylsuccinic acid. It then follows that the *gem*-dimethyl group which is present in eucarvone is also present in dihydroeucarvone; the presence of the double bond, however, prevents the determination of the constitution of the other part of the molecule. The ketone, when reduced with sodium and alcohol, yields dihydroeucarvol. Dihydroeucarvonoxime hydriodide, when reduced with sodium and alcohol, yields dihydroeucarvylamine, but with zinc dust and an alcoholic solution of hydrogen chloride at 0°, yields *tetrahydroeucarvone*, $C_{10}H_{18}O$, and this, when freed from unsaturated compounds by treatment with potassium permanganate, distils at 108—115° under a pressure of 20 mm. Its *oxime* does not crystallise, but its *semicarbazone*, $C_{11}H_{21}N_3O$, crystallises from ethylic acetate in fine needles melting at 191°, and is sparingly soluble in both ether and ethylic acetate. Tetrahydroeucarvone is not acted on by amylic nitrite and

hydrochloric acid, but the dihydroketone readily yields a bisnitroso-compound.

The theoretical quantity of cold 4 per cent. potassium permanganate oxidises tetrahydroeucarvone to the *ketonic acid*, which is best purified by conversion into its *semicarbazone*, $C_{11}H_{21}N_3O_2$ in the process of oxidation, about two-thirds of the ketone remains unaltered. The semicarbazone, which is sparingly soluble in the usual solvents with the exception of chloroform and acetic acid, crystallises from its warm ethylic acetate solution in long needles melting at 191°. The *oxime*, $C_{10}H_{19}NO_3$, of the ketonic acid crystallises in transparent, glistening prisms melting at 101—102°. The ketonic acid regenerated from the semicarbazone could not be obtained in a crystalline form ; that it is a methyl ketone was proved by its reaction with sodium bromide. The chief product of the oxidation of the ketone with cold permanganate is *gem*-dimethyl-adipic acid, $C_8H_{14}O_4$, crystallising from an ethereal light petroleum solution in prisms melting at 87—88° (compare Tiemann, this vol., i, 374). When the ketone (5 grams) is heated on the water bath for 18 hours with permanganate (66 grams) and water (1·5 litres), a mixture of acetic, oxalic, dimethylmalonic, and *gem*-dimethylsuccinic acids is obtained.

A hydrocarbon *euterpene* is obtained when dihydroeucarvol (100 grams) is treated with phosphorus pentachloride (200 grams), and the chloro-derivative thus formed, after removal of the phosphorus oxychloride, is boiled with quinoline for half an hour. This terpene boils at 161—165°, and when oxidised with permanganate yields acetic, oxalic, and *gem*-dimethylsuccinic acids.

Euterpene yields a dihydrobromide, which, when treated with bromine in the presence of iodine and then reduced in the manner previously described (this vol., i, 442), yields a hydrocarbon, 1 : 2 : 4-*dimethylethylbenzene*, boiling at 185—191°. The constitution suggested for euterpene is either

$$\begin{matrix} CH_2\cdot CH:CH \\ | \\ CMe:CH\cdot CH_2 \end{matrix}\!\!>CMe_2 \quad \text{or} \quad CMe\!\!<\!\!\begin{matrix} CMe:CH \\ CH\text{—}CH_2 \end{matrix}\!\!>CMe_2.$$

J. J. S.

Citral. By OSCAR DOEBNER (*Ber.*, 1898, **31**, 1888—1896).—The amount of citral present in various ethereal oils was determined by finding the amount of citrylnaphthacinchoninic acid,

$$C_{10}H_{16}\!\!<\!\!\begin{matrix} N\text{=====}C\cdot C_9H_{15} \\ \qquad\qquad | \\ C(COOH):CH \end{matrix},$$

they would yield when heated with pyruvic acid and β-naphthylamine in alcoholic solution (Abstr., 1894, i, 261, 532). Of those oils in which citral is known to occur, none contain more than an inconsiderable quantity, except lemon oil, from *Citrus limonum*, which contains 7—8, and lemon-grass oil, from *Andropogon citratus*, which contains 80—82 per cent.

The ketone obtained by the action of bleaching powder on lemon-grass oil and acetone in alcoholic solution, and "inverting" the pseudo-ketone thus obtained, by boiling it with a solution of sodium hydrogen sulphate (Fritsche and Co., English Patent, No. 26350), is shown conclusively to be nothing but the α-ionone of Tiemann and Krüger (Abstr., 1893,

i, 82; this vol., i, 376), mixed with a certain quantity of optically active terpenes and other substances not of an aldehydic nature (originally present in the lemon-grass oil), which confer optical activity on the mixture. As regards the reaction, the bleaching-powder is all destroyed in a few minutes, chloroform being formed; at this stage, the lemon-grass oil is still unchanged, however, and it is only by the subsequent action of the calcium hydroxide contained in the bleaching powder that it is converted into the pseudoketone.

C. F. B.

Oil of Violets from Oil of Lemon-grass. By J. ZIEGLER (*J. pr. Chem.*, 1898, [ii], **57**, 493—495).—The author calls attention to the fact (English Patent, No. 26350/96, &c.) that he has prepared a ketone similar to, but different from, pseudoionone by heating lemon-grass oil, or, better, those fractions of it which contain but little citral, with acetone, bleaching powder, dilute alcohol, and a little cobalt nitrate. By boiling this product for several days with a solution of sodium hydrogen sulphite, it is possible to convert it into an isomeride, which resembles ionone, but is not identical with that substance; it has been put on the market as "artificial oil of violets." C. F. B.

[NOTE BY ABSTRACTOR.—Doebner (preceding abstract) appears to have shown that the two substances in question are nothing else than impure pseudoionone and ionone. The discrepancy awaits explanation.]

Ionone from Lemon-grass Oil. By J. C. W. FERDINAND TIEMANN (*Ber.*, 1898, **31**, 2313—2329).—It is shown in this paper that citral is the only considerable aldehydic constituent of lemon-grass oil. The author replies in detail to the criticisms of Ziegler (preceding abstract) on his previous communications (this vol., i, 374).

M. O. F.

Amidoborneol. By PAUL DUDEN and ALFRED E. MACINTYRE (*Ber.*, 1898, **31**, 1902—1904).—When amidocamphor (Claisen and Manasse, Abstr., 1893, i, 479) is reduced in boiling alcoholic solution with excess of sodium, it yields *amidoborneol*, $C_{10}H_{19}NO$, which melts at 187°, boils at 264° under a pressure of 751 mm., and shows a tendency to sublime; it also crystallises with water, and then melts at about 90°. Its *hydrochloride* decomposes at 285°, the yellowish *platinochloride* at 272°, the *aurochloride* at 190°; the yellow *picrolonate* (Abstr., 1897, i, 314) melts and decomposes at 272°; the *carbamide* melts at 177°, the *acetyl* derivative at 170°; the *methiodide* decomposes above 270°. C. F. B.

A Crystalline Heptacetin derived from Ouabin. By ALBERT ARNAUD (*Compt. rend.*, 1898, **126**, 1654—1656).—When finely-powdered anhydrous ouabin, $C_{30}H_{46}O_{12}$, is gently warmed with acetic anhydride and a little zinc chloride, it loses a molecule of water and is converted into a crystalline *heptacetate*, which analysis shows to have the composition $C_{30}H_{37}Ac_7O_{11}$. At the same time, a large proportion of an amorphous acetyl compound is produced, which is very soluble in alcohol and other solvents, and appears to be derived from a substance resulting from a more advanced dehydration of ouabin. The crystal-

line heptacetate is almost insoluble in water and in ether, slightly soluble in cold alcohol and acetic acid, readily in ethylic acetate, acetone, and hot alcohol. It crystallises in thin, rhombic, anhydrous plates which melt and decompose rapidly at about 310°. The alcoholic solution is lævorotatory, $[\alpha]_D = -68{\cdot}5°$ at 85°. The heptacetate is converted by hydrolysis with alkalis into an amorphous *acid* substance which resembles ouabaic acid in its properties, but differs from it in possessing a much lower rotatory power. This acid, when boiled with dilute mineral acids, yields an insoluble resin and a considerable quantity of rhamnose. From these results, it follows that the molecule of ouabin contains nine hydroxyl groups; four of these belong to the rhamnose molecule, whilst the other five, connected in an as yet unknown manner, lose a molecule of water previous to the formation of the heptacetate. N. L.

Jalapinolic Acid. By Nicolai Kromer (*J. pr. Chem.*, 1898, [ii], **57**, 448—466).—Jalapic acid was prepared from false jalap resin, and boiled with dilute hydrochloric acid; the jalapinolic acid, $C_{16}H_{32}O_3$, thus obtained was purified by converting it into its methylic or ethylic salt and recrystallising these first from light petroleum and then from ether; they melt at 50—51° and 47—48° respectively, and solidify at 43—42° and 41—40°; the purified acid melts at 67—68°, and is optically inactive; the silver salt was analysed.

When the ethylic salt is heated with acetic anhydride and sodium acetate, a *monacetyl* derivative is formed, which boils at 224—225° under 50 mm. pressure.

Jalapinolic acid forms no additive product with bromine, but yields a liquid substitution product, which, however, was found not to be homogeneous.

When the methylic salt is mixed with phosphorus iodide and the mixture is moistened with hydriodic acid and allowed to remain for 24 hours, the product being finally reduced with zinc and hydrochloric acid in boiling alcoholic solution, an *acid*, $C_{16}H_{32}O_2$, is obtained, melting at 65—66°, solidifying at 63—62°, and having the character of a saturated compound; it is not identical with any of the acids of this composition already known.

When the acid (1 mol.) is oxidised with potassium permanganate (4 atoms) in alkaline solution at 50°, methylethylacetic acid, sebacic acid, and an acid melting at 89—91°, and possibly isomeric with sebacic acid, are formed.

Probably, then, jalapinolic acid has the constitution

$$CHMeEt{\cdot}CH(OH){\cdot}C_{10}H_{20}{\cdot}COOH.$$

C. F. B.

Lupulinic Acid. By Georg Barth and Carl J. Lintner (*Ber.*, 1898, **31**, 2022—2025).—Hop resin yields two crystalline substances having a bitter taste and a slightly acidic nature; they are termed α- and β-hop-bitter acids. The latter is identical with Bungener's lupulinic acid, obtained by extracting lupulin with light petroleum. To remove all traces of waxy and resinous substances, the acid is repeatedly crystallised from light petroleum and finally from 90 per cent. methylic alcohol; from the latter solvent, it crystallises in

glistening prisms which melt at 92° and become resinous on exposure to the air. The mean of ten analyses gave C = 75·0; H = 9·17 per cent., which correspond with the formula $C_{25}H_{36}O_4$; Bungener supposed the acid to have the formula $C_{25}H_{35}O_4$, and in Beilstein's handbook the double formula, $C_{50}H_{70}O_8$, is given. Determinations of the molecular weight by the depression of the freezing point, the rise in boiling point, and titration with standard alkali, all give numbers closely approximating to the simple formula $C_{25}H_{36}O_4$.

The acid reduces ammoniacal silver solutions, and when oxidised with permanganate in alcoholic solution valeric acid is formed; it does not give crystalline derivatives with phenylhydrazine, semicarbazide, or hydroxylamine. The authors believe that both the above α- and β-hop-bitter acids are derived from the terpenes, and stand in close relationship to the other ingredients of the oil of hops.

G. T. M.

Yohimbine. By OBERWARTH (*Virchow's Archiv*, 1898, **153**, 292—305).—An extract of the acid of the rind of the yohimbehe has been recommended as an aphrodisiac. Two substances named yohimbine and yohimbenine have been separated from it. The physiological action of the latter is weaker than, but is otherwise similar to, that of the former. Yohimbine is an alkaloid melting at 234°; its hydrochloride melts at 287°. It produces paralysis of the nervous system after preliminary convulsions. It weakens, then stops the heart; blood pressure falls. Death is produced by paralysis of the respiratory apparatus. (Compare this vol., i, 455.) W. D. H.

Lichens and their Characteristic Constituents. By OSWALD HESSE (*J. pr. Chem.*, 1898, [ii], **57**, 409—447. Compare this vol., i, 531).—*Parmelia perlata* (L) Ach. = *Imbricaria perlata* Körber.—A specimen from the neighbourhood of Stuttgart contained atranorin only. Another, from American cinchona bark, contained usnic acid and atranorin, and a little vulpic acid; the atranorin was erroneously described as a new substance, parmelin, in an earlier paper (Abstr., 1895, i, 299). A third specimen, from Java cinchona bark, contained atranorin and lecanoric acid; the varieties with grey thallus contained very little of this acid, those with a greenish-grey thallus, which become coloured by bleaching powder solution, contained more. In one sample, the atranorin was found to be accompanied by a new substance, *perlatin*, $C_{19}H_{14}O_5(OMe)_2$, which can be dissolved out with alcohol. This crystallises in pale yellow prisms; hydriodic acid eliminates the methyl from it, forming crystalline *norperlatin*, which begins to sublime at 250° and melts at 274° and has not the character of an acid.

P. physodes (L) Ach. = *P. ceratophylla* (Wallroth) = *Imbricaria physodes* Körber, from the neighbourhood of Stuttgart.—From the ethereal extract, atranorin and capraric acid first crystallised, extraction with potassium hydrogen carbonate solution dissolving out the latter. By extracting the ethereal mother liquor with potassium hydrogen carbonate solution, capraric acid (see under *P. caperata*) and physodic acid were obtained, and were separated by treatment with lime- or strontia-water, which yield insoluble salts with capraric acid. Final

evaporation of the ethereal solution yields an amorphous substance, *physol*, $C_{20}H_{24}O_5$, which melts at about 145°, contains no methoxyl, has the characters of an alcohol, and, in alcoholic solution, oxidises spontaneously to physodic acid. *Physodic acid*, probably $C_{19}H_{19}O_2(OH)_2\cdot COOH$, which melts and decomposes at 190—192°, contains no methoxyl; it forms a *diacetyl* derivative melting at 158°, and a series of ill-defined salts. When boiled with baryta solution, it loses carbonic anhydride, and yields a product obtained only as a reddish syrup, whilst prolonged boiling with alcohol, ether, or other organic solvents converts the acid into an amorphous isomeride. The ceratophyllin formerly found in this acid was methylic betorcinolcarboxylate, and had been formed by the action of the hot sodium carbonate solution on the atranorin. The substance described as physodin was probably slightly impure capraric acid.

P. caperata (L.) Ach. = *Imbricaria caperata*, Körber, from Stuttgart and Heidelberg.—From the ethereal extract, capraric acid separated first, mixed with usnic acid, which could be dissolved out with benzene; caperatic acid remained in solution. In specimens that had grown on oak trees, caperin and caperidin separated out in addition; these remain when the whole mixture is extracted with potassium carbonate solution, and can be crystallised from alcohol or benzene, from which the caparidin separates first. *Capraric acid*, $C_{22}H_{18}O_8(COOH)_2$, crystallises in white needles, which begin to decompose at about 240°; the amorphous *barium* salt was analysed. When treated with boiling acetic anhydride, the acid yields an amorphous *anhydride*, $C_{24}H_{18}O_{11}$; and if boiled with alcoholic potash, a substance is formed which loses carbonic anhydride when heated with hydrochloric acid, yielding *capranic acid*, presumably $C_{23}H_{20}O_{10}$, and this, when dried at 100°, loses water and forms *capranide*, $C_{46}H_{38}O_{19}$. *Caperatic acid*, $COOMe\cdot C_{18}H_{33}O_2(COOH)_2$, is crystalline, and melts at 132°; the amorphous *barium* and *silver* salts were analysed; when heated with acetic anhydride, it forms an anhydride, *caperatide*, which is crystalline and melts at 47°; when heated with hydriodic acid, it loses methoxyl, and forms tribasic *norcaperatic acid*, which melts at 138°, crystallises with $2H_2O$, and perhaps contains two hydroxyl groups; the amorphous *barium* salt of this acid was analysed. *Caperin*, $C_{36}H_{60}O_3$, is a crystalline substance which melts at 243°, and has a very inert character; neither strong sulphuric, nitric, nor hydriodic acid reacts with it. When heated for 24 hours with absolute alcohol at 150°, it forms *dicaperin hydrate*, $C_{72}H_{120}O_6 + H_2O$, which melts at 227—228°, and when a solution of caperin in benzene is evaporated rapidly, *dicaperin*, $C_{72}H_{120}O_6$, melting at 248—250°, is deposited in slender needles. Molecular weight determinations in chloroform solution, by the boiling point method, show that this substance dissolves at first with the double molecular weight, but after a time suddenly dissociates into caperin; any further quantity of dicaperin now added to the solution is at once dissociated. *Caperidin*, $C_{24}H_{40}O_2$, is crystalline and melts at 262°; it is also a chemically inert substance.

P. conspersa (Ehrh.) Ach. = *Imbricaria conspersa* Körber.—Usnic acid, and another acid not identified and possibly identical with Zopf's salazinic acid (this vol., i, 90).

Physcia stellaris (L.) *f. adscendens* (Fr.) Th. Fr.—Atranorin only (compare Zopf, *P. tenella*, Abstr., 1896, i, 103).

Xanthoria parietina (L.) Th. Fr. = *Parmelia parietina* (Ach.), *Physcia parietina* (Nyl.).—The physciol and physcianin previously found in this lichen (Abstr., 1895, i, 300) were not present originally, but were formed by the action of the hot sodium carbonate solution on the atranorin. Atranorin predominates in pale yellow to green specimens that have grown in the shade and in moist places; physcion in bright yellow specimens. Heating with hydriodic acid, or with a mixture of hydrochloric and acetic acids, eliminates methyl from physcion, forming protophyscion. The further action of hydriodic acid leads to the formation of protophyscihydrone, $C_{15}H_{12}O_4$, which is also the product of the action of zinc powder on protophyscion. Prolonged heating with methyl alcoholic potash and methylic iodide converts physcion into two isomeric *methylphyscions*, $C_{15}H_8Me_2O_5$; the α-compound is yellow and melts at 205°, whilst the β-compound is red, melts at 178°, and is more soluble than the other in acetic acid.

X. lychnea (Ach.) Th. Fr.—Physcion only.

X. Candelaria (Ach.) from Berchtesgaden, Brand in the Vorarlberg, and Stuttgart.—Physcion only.

Candelaria concolor (Dicks.) Th. Fr., from Stuttgart, &c.—Dipulvic acid, $C_{36}H_{22}O_9$; this forms red needles and melts at 211°; heated with acetic anhydride, it yields yellow pulvic anhydride, $C_{18}H_{10}O_4$, melting at 214°, and after crystallisation from benzene, at 220°. The calycin found by Zopf (Abstr., 1895, i, 298) was dipulvic acid; the ethylpulvic acid (this vol., i, 90) was formed by the action on the dipulvic acid of small quantities of alcohol present in the ether used.

Sticta pulmonaria (L.) Schaerer.—Protocetraric acid.

Nephromium lævigatum (Ach.) Nylander, and *N. tommentosum* (Hoffm.) Nylander, from Nyborg in Finmark.—The ether extract leaves a residue from which light petroleum removes a wax-like substance; when what remains is crystallised from benzene, usnic acid crystallises first, and then a new substance, *nephrin*, which melts at 168° and appears to be a diterpene hydrate, $C_{20}H_{32} + H_2O$.

N. lusitanicum (Schaerer) from the island of Miquelon and from Brittany.—The ether extract gave a residue which was recrystallised from acetic acid; nephrin separated first, and then a new substance, nephromin, $C_{16}H_{12}O_6$ ($= C_{15}N_9O_5 \cdot OMe$?), mixed with some wax, which was removed with light petroleum. *Nephromin*, which is ochre-coloured, melts and decomposes at about 196°. With alkalis, it forms red solutions, in which it ultimately becomes transformed into an amorphous substance; it is closely related to physcion.

Gasparrinia medians (Nylander) = *Physcia medians* (Nyl).—Calycin and rhizocarpic acid; no ethylpulvic acid (Zopf, Abstr., 1895, i, 298).

G. elegans (Lk.) Tornab. = *Amphiloma elegans* Körber = *Physcia elegans* Nylander, from the neighbourhood of Stuttgart and of Salzburg, and from the Vorarlberg.—Physcion only.

G. murorum (Hoffm.) Tornab. = *Amphiloma murorum* Körber, from Stuttgart.—Physcion only.

G. decipiens Arnold, from Stuttgart.—Physcion only.

C. F. B.

The Chemistry of Chlorophyll. By G. BODE (*J. pr. Chem.*, 1898, [ii], **57**, 488—493). A reply to Marchlewski (this vol., i, 536).

Colouring Matter of Cochineal. By CARL LIEBERMANN (*Ber.*, 1898, **31**, 2079—2084).—Carminic acid is probably an indene derivative having the composition $C_{22}H_{22}O_{13}$ (compare Abstr., 1897, i, 539 and 540); the author is engaged in the study of its derivatives, and of its products of decomposition. The acid, which is itself readily soluble in water, readily passes into insoluble colouring matters, the change being accompanied by an elimination of water and an increase in molecular complexity; this change is characteristic of the keto-indene series (Abstr., 1887, 587, and 1889, 1067). With a view to studying the properties of similarly constituted compounds, the author condenses dibromindone with diethylic malonate in the presence of sodium ethoxide. The condensation product which results from the combination of dibromindone and diethylic malonate, in molecular proportion, is provisionally termed *diethylic bromindonemalonate*; it crystallises from dilute alcohol in yellow leaflets and melts at 129—130°. Purple colorations are developed with alcoholic and aqueous alkalis, but it does not dye wool either with or without mordants. Its constitution may be either $C_6H_4{<}{\scriptstyle -CO- \atop CBr}{>}C{\cdot}CH(COOEt)_2$ or $CO{<}{\scriptstyle CBr \atop C_6H_4}{>}C{\cdot}CH(COOEt)_2$.

Ethylic bromindoneacetoacetate, $C_{15}H_{13}BrO_4$, is similarly prepared, melts at 80—82°, and gives similar colorations with alkalis.

Neither Roser's hydroxybromindone, $C_6H_4{<}{\scriptstyle -CO- \atop C(OH)}{>}CBr$, nor α-, nor β-bromocarmin yield colouring matters with diethylic malonate.

G. T. M.

Ethereal Indoxylates. By DANIEL VORLÄNDER and RUDOLF VON SCHILLING (*Annalen*, 1898, **301**, 349—352. Compare Blank, this vol., i, 589).—Ethereal salts of phenylglycine-carboxylic acid are converted into ethereal indoxylates, $C_6H_4{<}{\scriptstyle -NH- \atop C(OH)}{>}C{\cdot}COOR$, when gently heated with sodium ethoxide.

Dimethylic phenylglycine-orthocarboxylate crystallises in elongated leaflets, and melts at 97°; the *diethylic* salt melts at 75°. On heating these compounds, dissolved in benzene or ether, with sodium ethoxide, the corresponding salts of indoxylic acid are formed.

Methylic indoxylate melts at 155—157°. M. O. F.

The Base prepared by E. Fischer from Methylketol and Methylic Iodide. By KARL BRUNNER (*Ber.*, 1898, **31**, 1943—1949. Compare this vol., i, 384; also Plancher, this vol., i, 536).—Just as Fischer's base is obtainable from methylisopropylmethylphenylhydrazone, the hydriodide of 1′-phenyl-3′:3′-dimethyl-2′-methyleneindoline, $C_6H_4{<}{\scriptstyle CMe_2 \atop NPh}{>}C{:}CH_2$, is produced by the action of alcoholic hydrogen iodide on methylisopropyldiphenylhydrazone.

The *hydriodide*, $C_{17}H_{17}N,HI$, which crystallises from boiling 90 per cent. alcohol in pale yellow prisms, melts at 192°, and decomposes at 195°, evolving gas. The salt dissolves with difficulty in cold water,

but is freely soluble in hot water, forming a turbid solution. 1′-*Phenyl*-3′ : 3′-*dimethyl*-2′-*methyleneindoline* boils at 183—185° under a pressure of 32 mm., and does not solidify at −10°. It is a colourless oil having a spice-like odour, and resembles Fischer's base, not only in the property of becoming magenta red when exposed to air, but also in the formation of a yellow, oily precipitate gradually becoming crystalline, which is produced when ferric chloride is added to the solution in hydrochloric acid. The *picrate* forms yellow leaflets, and melts at 111°; the *sulphate* crystallises in needles, and melts at 206°, above which temperature it decomposes and evolves gas.

M. O. F.

Condensations of Isatic Acid with Formation of Derivatives of Cinchonic Acid. By C. ENGELHARD (*J. pr. Chem.*, 1898, [ii], 57, 467—484. Compare Pfitzinger, this vol., i, 207).—Isatic acid, $NH_2 \cdot C_6H_4 \cdot CO \cdot COOH$, prepared by boiling isatin with 30 per cent. potash, condenses with dibenzyl ketone when the latter and some alcohol are added to the alkaline solution of isatic acid, and the whole is boiled for several hours. The product is 3′-*phenyl*-2′-*benzylquinoline*-4′-*carboxylic acid* [quinoline-4′-carboxylic acid = cinchonic acid]; it melts at 293—295°, and has feeble basic, but more pronounced acid properties; its *silver* salt was analysed; when heated alone or with soda lime, it yields 3′-*phenyl*-2′-*benzylquinoline* as an oil; its orange-yellow *platinochloride* melts at 208°, and crystallises with $2H_2O$.

With ethylic benzoylacetate, isatic acid condenses, in alkaline solution at the ordinary temperature, to 2′-*phenylquinoline*-3′ : 4′-*dicarboxylic acid*, which melts at 193—194°, and crystallises with $2H_2O$; the *silver* salt was analysed.

With levulinic acid, isatic acid condenses in boiling, alkaline solution to 4′-*carboxy*-2′-*methylquinoline*-3′-*acetic acid*,

$$C_6H_4 < \begin{matrix} C(COOH) \\ N = CMe \end{matrix} > C \cdot CH_2 \cdot COOH \ ;$$

this begins to decompose at about 280°; the *silver* salt was analysed. When distilled with soda-lime, the acid yields 2′ : 3′-dimethylquinoline (Rhode, Abstr., 1887, 974; 1889, 523). As the CH_3-group in levulinic acid standing at the end of the chain has not reacted, probably the same would hold for acetoacetic acid, and if so, the compound prepared by Pfitzinger from this acid and isatic acid would be 2′-methylquinoline-3′ : 4′-dicarboxylic acid, and not the 2′ : 4′-dicarboxylic acid.

Paramethylisatic acid reacts with ethylic acetoacetate in cold alkaline solution, and the 3 : 2′-*dimethyl*-3′ : 4′-*dicarboxylic acid* thus formed melts at 233—234°; its *silver* salt, with $2H_2O$, is very hygroscopic.

Isatic acid in cold alkaline solution condenses with ethylic acetonedicarboxylate, forming 3′(or 4′)-*carboxy*-2′-*methylquinoline*-2′-*acetic acid*, carbonic anhydride being liberated. The acid, which is pale yellow, melts at 228—229° and crystallises with $1H_2O$; the *silver* salt was analysed.

Attempts to prepare quinoline-2′ : 3′ : 4′-tricarboxylic acid, by condensing isatic acid in alkaline solution with ethylic oxalacetate, and

by oxidising Pfitzinger's methylquinolinedicarboxylic acid with chromic and sulphuric acids, were unsuccessful. In the first case, the oxalacetate was decomposed and the isatic acid remained unchanged; in the second, most of the dicarboxylic acid was completely oxidised and the rest remained unchanged. C. F. B.

Synthesis of *d*- and *l*-Ethylpiperidine. By ADOLF GÜNTHER (*Ber.*, 1898, **31**, 2134—2142).—*Ethylic γ-phenoxypropylethylmalonate*, $OPh\cdot CH_2\cdot CH_2\cdot CH_2\cdot CEt(COOEt)_2$, prepared by acting on ethylic γ-phenoxypropylmalonate with sodium and ethylic iodide, forms a colourless syrup boiling at 227—230° under a pressure of 22—23 mm. *γ-Phenoxypropylethylmalonic acid*, $OPh\cdot C_3H_6\cdot CEt(COOH)_2$, is formed when the ethylic salt is treated with potash; it dissolves readily in the ordinary solvents with the exception of water, and crystallises from ether in fine, prismatic needles which melt at 89—90°, and rapidly loses carbonic anhydride at 140—200°. A solution of the ammonium salt gives a white precipitate with calcium chloride, and a bright green, indistinctly crystalline precipitate with copper sulphate; the copper salt melts and decomposes at 231—233°, whilst the silver salt forms a white, amorphous powder.

δ-Phenoxy-α-ethylvaleric acid, $OPh\cdot C_3H_6\cdot CHEt\cdot COOH$, formed from phenoxypropylethylmalonic acid when it is heated at 140—200°, boils at 322—323° and forms stellate groups of needles melting at 60—63°; it dissolves readily in alcohol and ether, and may be crystallised from light petroleum. When heated with lead thiocyanate at 200—220°, it yields *δ-phenoxy-α-ethylvaleronitrile*, $OPh\cdot C_3H_6\cdot CHEt\cdot CN$, which boils at 315—317°.

ε-Phenoxy-β-ethylamylamine, $OPh\cdot C_3H_6\cdot CHEt\cdot CH_2\cdot NH_2$, obtained by reducing phenoxyethylvaleronitrile with sodium and alcohol, has the odour characteristic of fatty amines, and yields a semi-crystalline *hydrochloride*, and a *picrate*, $C_{19}H_{24}O_8N_4$; this crystallises in fine, lemon-yellow needles, and melts at 104—106° to a reddish-yellow, transparent liquid which, on cooling, sets to a mass of leaflets.

ε-Chlor-β-ethylamylamine, $C_3H_6Cl\cdot CHEt\cdot NH_2$, is formed when the hydrochloride of phenoxyethylamylamine is heated with hydrochloric acid at 100° during 20 hours. The *picrate*, $C_7H_{16}ClN,C_6H_3N_3O_7$, crystallises in fine, yellow needles melting at 145°; the *platinochloride*, $(C_7H_{17}NCl)_2PtCl_4$, forms microscopic, yellow needles which blacken at 225°, and decompose at 242—244°.

When chlorethylamylamine is heated with excess of potash in closed vessels on the water bath, it loses hydrogen chloride and yields β-ethylpiperidine; this is isolated by steam distillation, neutralisation of the distillate with hydrogen chloride, and evaporation to dryness. The hydrochloride thus obtained, as well as the picrate and platinochloride, have the same melting points and properties as those formed from Stoehr's base (Abstr., 1892, 628). The free base is a transparent, limpid liquid of coniine-like odour, boiling at 154—155°; it fumes in the air and has a sp. gr. = 0·871 at 16°/4°. Its physiological properties resemble those of β-propylpiperidine (Abstr., 1897, i, 437), but are much less marked.

The resolution of β-ethylpiperidine into its optical antipodes was

accomplished by Marckwald's method (Abstr., 1896, 42). l-*β-Ethylpiperidine* d-*hydrogen tartrate* crystallises in fine tablets or needles, and melts to a brown liquid at 169—170°. l-*β-Ethylpiperidine* boils at 155° and has a rotation $[\alpha]_D = -4{\cdot}51°$ at 15°; its *hydrochloride* forms silky needles and melt at 142°. d-*β-Ethylpiperidine* l-*hydrogen tartrate* forms plates which turn to feather-like crystals, and melt at 174° to a brown liquid. d-*β-Ethylpiperidine* is dextrorotatory, and affords a *hydrochloride* which melts at the same temperature as that made from the lævo-base. A. L.

Some Bases Derived from Piperidine. By GUSTAVE ANDRÉ (*Compt. rend.*, 1898, **126**, 1797—1799).—Ethylenedipiperidine, $C_2H_4(C_5NH_{10})_2$, and also the dihydrobromide of this base, have been already described by Brühl. The *dihydrochloride*, which is readily formed by the action of ethylenic chloride on piperidine, crystallises in fine needles, and when boiled with aqueous potash, is converted into ethylenedipiperidine; the latter is also easily prepared by boiling a mixture of ethylenic bromide (1 mol.) and piperidine (2 mols.) with excess of aqueous potash in a reflux apparatus. Ethylenedipiperidine was thus obtained as a colourless oil having a faint odour of piperidine; it boils at 261° under a pressure of 760 mm., and has a sp. gr. = 0·9364 at 0°. Brühl describes this base as becoming solid at 4°, but the author was unable to solidify it even at −23°. Ethylenedipiperidine readily combines with water to form a *hydrate* of the composition $C_2H_4(C_5NH_{10})_2 + 3H_2O$, which melts and dissociates on heating. Attempts were made to prepare a base isomeric with ethylenedipiperidine by the action of ethylidenic chloride or bromide on piperidine. The products obtained appear, however, to be mixtures of various compounds, and such a base, if it exists at all, is probably very unstable.

Methylethylenedipiperidine, $C_5NH_{10}{\cdot}CHMe{\cdot}CH_2{\cdot}C_5NH_{10}$, obtained by the action of aqueous potash on a mixture of propylenic bromide with piperidine, is an oily liquid boiling at 268—269° under a pressure of 745 mm., and having a sp. gr. = 0·9225 at 16°; it does not solidify when cooled to the temperature of boiling methylic chloride. It is nearly insoluble in water, but forms with it a crystalline *hydrate* which is only stable at a low temperature.

Trimethylenedipiperidine, $CH_2(CH_2{\cdot}C_5NH_{10})_2$, which has been previously prepared by Töhl, was obtained by the action of trimethylenic bromide on piperidine in presence of potash, as a liquid boiling at 278—279° under a pressure of 752 mm., and having a sp. gr. = 0·9183 at 16°; it does not solidify at −23°. When shaken with a little water and cooled, it forms a crystalline *hydrate* of the composition $C_3H_6(C_5NH_{10})_2 + 8H_2O$, which dissociates at the ordinary temperature.

Trimethylenoldipiperidine, $OH{\cdot}CH(CH_2{\cdot}C_5H_{10})_2$, is obtained when *α*-dibromhydrin is warmed with piperidine in presence of aqueous potash; it boils at 171—172° under a pressure of 15 mm., and has a sp. gr. = 0·9812 at 15°.

Methylolethylenedipiperidine, $C_5NH_{10}{\cdot}CH_2{\cdot}CH(CH_2{\cdot}OH){\cdot}C_5NH_{10}$, from *β*-dibromhydrin and piperidine, boils at 178—180° under a pressure of 23 mm., and has a sp. gr. = 0·9877 at 15°. It resembles

the preceding compound in forming a well-crystallised platinochloride, and in not yielding a hydrate by prolonged agitation and cooling with water. N. L.

Syntheses in the Piperidine Series. By FELIX B. AHRENS (*Ber.*, 1898, 31, 2272—2276. Compare Abstr., 1897, i, 368).—The base, $C_{10}H_{18}N_2$, obtained by the electrolysis of nitrosopiperidine yields a *dithiocarbanilide*, $C_{10}H_{16}N_2(CS\cdot NHPh)_2$, melting at 183°, and an oily *monobenzoyl* derivative, which, on further treatment with benzoic or acetic anhydride, gives rise to tarry products. Two isomeric *bases*, $C_5H_{11}N$, differing markedly from piperidine, are produced from the above diamine, on reduction with tin and hydrochloric acid; the α-base, its salts, and its benzene sulphonamide are oily, whilst the β-base and its derivatives are solids, the *benzenesulphonamide* melts at 160°.

Amido-acids are also produced by the electrolytic oxidation of nitrosopiperidine in sulphuric acid; an acid which was not definitely characterised has been previously mentioned, and a second *acid* has now been obtained by treating the product of electrolysis with barium hydroxide and carbonic anhydride successively, evaporating to dryness the filtrate from the barium carbonate, and liberating the acid with sulphuric acid. Neither the acid nor its metallic salts could be obtained crystalline, but a well-defined *platinochloride* crystallising from water in yellow leaflets, and melting at 170°, indicates that the acid is an amidovaleric acid.

Two volatile bases are also produced in this reaction, and are distilled off from the above product of electrolysis after it has been rendered alkaline with barium hydroxide; they are separated by means of their aurochlorides. Both of these salts have the composition $(C_5H_{11}N),HAuCl_4$; the less soluble melts at 206°, and the free base is found to be identical with piperidine; the more soluble aurochloride melts at 213°. G. T. M.

Electrolysis of Nitroso-α-pipecoline and Nitrosotetrahydroquinoline. By RICHARD WIDERA (*Ber.*, 1898, 31, 2276—2278. Compare previous abstract).—A solution of nitroso-α-pipecoline in 30 per cent. sulphuric acid, electrolysed at the anode of an electrolytic cell, yields an *amidocaproic* acid of unknown constitution; its hydrochloride melts at 196°, and its platinochloride at 204°.

When the product of electrolysis is rendered alkaline and steam distilled, the distillate contains ammonia, α-pipecoline, and an oily *diamine*, which yields a *monothiocarbanilide*, $C_{12}H_{23}N_2\cdot CSNHPh$, melting at 116°.

The electrolysis of nitrosotetrahydroquinoline at the anode yielded only tetrahydroquinoline. G. T. M.

Syntheses in the Piperidine Series. III. By FELIX B. AHRENS (*Ber.*, 1898, 31, 2278—2280).—It is well-known that pyridine bases are converted into derivatives of dipyridyl under the influence of sodium. The author has found that when the metal is suspended in a solution of nitrosopiperidine in dry ether, γ-dipiperidyl is produced, along with a small proportion of piperylhydrazine. Benzoylpiperidine yields piperidine, benzoic acid, and two compounds having the em-

pirical formulæ of benzoyldipiperidyl and dibenzoyldipiperidyl respectively. M. O. F.

aaa'a'-**Tetramethyldipyridyl.** By FRANZ HUTH (*Ber.*, 1898, **31**, 2280—2282).—2 : 6-Dimethylpyridine resists the action of metallic sodium at the temperature of boiling water, but when heated with it in sealed tubes at 180—200° during 8—10 hours, yields *aaa'a'-tetramethyldipyridyl*, $C_{14}H_{16}N_2$, which crystallises from boiling water in long, white needles, and melts at 148—149°. The *platinochloride* crystallises in long, reddish-yellow needles, and does not melt below 280°; the *picrate* also forms long, yellow needles, and blackening at 230°, intumesces at 273°. The *aurichloride* and *mercurichloride* decompose at 216° and 280° respectively. *Dipyridyltetracarboxylic acid*, $C_{14}H_{12}N_2(COOH)_4$, is obtained on oxidising tetramethyldipyridyl with potassium permanganate. M. O. F.

Synthetical Alkines of the Pyridine and Piperidine Series. By ALBERT LADENBURG [and in part MEISSNER and THEODOR] (*Annalen*, 1898, **301**, 117—153).—1-Methylpipecolylalkine [1-methyl-2-hydroxyethylpiperidine], $CH_2<\begin{matrix}CH_2-CH_2\\CH_2\cdot NMe\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot OH$, was first prepared by the author (Abstr., 1890, 67) from α-pipecolylalkine, the reduction product of α-picolylalkine, obtained by the action of formaldehyde on α-picoline. A substance of the same composition was subsequently obtained by Lipp (Abstr., 1892, 1245), who submitted 1-methyltetrahydropicoline to the action of formaldehyde, and reduced the product; the fact that the two compounds are not identical was ascribed to the presence of impurities in the specimen prepared by Ladenburg. The latter, however, showed that this could not be the true explanation (Abstr., 1893, i, 426), and subsequently suggested the influence of asymmetric nitrogen as the cause of isomerism (Abstr., 1897, i, 437). This view must in turn be abandoned, the author having found that the two alkines are structurally different, the action of formaldehyde on 1-methyltetrahydropicoline yielding 1 : 2-dimethyl-3-hydroxymethyl-Δ^2-tetrahydropyridine, $CH_2<\begin{matrix}C(CH_2\cdot OH){:}CMe\\CH_2\text{———}CH_2\end{matrix}>NMe$, instead of 1-methyl-2-hydroxyethyl-Δ^2-tetrahydropyridine (Abstr., 1897, i, 229).

A detailed account is given of several compounds described in the author's first paper on this subject (Abstr., 1890, 67), along with new bases of the same type.

1-*Ethylpipecolylalkine* [1-*ethyl-2-hydroxyethylpiperidine*],

$$CH_2<\begin{matrix}CH_2\cdot NEt\\CH_2\cdot CH_2\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot OH,$$

is prepared by heating pipecolylalkine with an aqueous solution of potassium ethyl sulphate; it is a colourless, viscous liquid, which boils at 241·5 (corr.), and has the sp. gr. = 0·9766 at 17°. The *mercurichloride* crystallises in colourless rhombohedra, containing $3H_2O$, and melts at 180—181°. The *platinochloride* of the ethylammonium base crystallises in small, orange prisms, and melts at 210°.

1 : 2-*Ethylvinylpiperidine*, $CH_2<\begin{matrix}CH_2\cdot NEt\\CH_2\cdot CH_2\end{matrix}>CH\cdot CH{:}CH_2$, is obtained

by heating a solution of the alkine in glacial acetic acid with concentrated sulphuric acid at 175—180°; it boils at 173—178° under a pressure of 754 mm. The *platinochloride* melts at 205·5°.

Propylpipecolylalkine [*2-hydroxyethyl-1-propylpiperidine*], $C_{10}H_{21}NO$, is a viscous liquid which boils at 246°, and does not solidify at −14°; it has a sp. gr. = 0·9578 at 20°/4°. The *mercurichloride* and *platinochloride* of the methylammonium base melt at 157° and 194·5° respectively. *1-Isopropylpipecolylalkine* [*2-hydroxyethyl-1-isopropylpiperidine*] boils at 235—239°, and has a sp. gr. = 0·9597 at 20°; the *mercurichloride* and *platinochloride* of the methylammonium base melt at 198° and 182° respectively.

1-Benzylpipecolylalkine [*1-benzyl-2-hydroxyethylpiperidine*], $C_{14}H_{21}NO$, boils at 318—321°, and has a sp. gr. = 1·0343 at 4°. *1-Methylpipecolylmethylalkine* [*1-methyl-2-β-hydroxypropylpiperidine*], $C_9H_{19}NO$, is a strongly alkaline liquid which solidifies in liquid air, and melts in solid carbonic anhydride; the *mercurichloride* and *platinochloride* melt at 150—155° and 203—204° respectively.

1 : 3-*Methylethylpiperidine*, $C_8H_{17}N$, is prepared by reducing with tin and hydrochloric acid the base erroneously described by Lipp as methylvinylpiperidine (Abstr., 1897, i, 230); it is a colourless liquid having the odour of piperidine, boils at 153·1° (corr.) under a pressure of 756 mm., and has a sp. gr. = 0·8394 at 0°. The *hydrochloride* crystallises in long, colourless prisms, and melts at 174—176°; the *aurichloride* forms needles, and melts at 104—105°. Distillation of the hydrochloride in an atmosphere of hydrogen chloride yields β-ethylpiperidine, from which β-pyridine is obtained on distilling the hydrochloride with zinc dust. M. O. F.

Hydrogenisation of Nicotyrine. By AMÉ PICTET and PIERRE CRÉPIEUX (*Ber.*, 1898, **31**, 2018—2022).—The authors endeavour to accomplish the final stage in the synthesis of nicotine by the partial hydrogenisation of nicotyrine, the methiodide of which has been synthetically prepared (Abstr., 1895, i, 627).

Iodonicotyrine, produced on shaking nicotyrine with a solution of iodine in dilute soda, acidifying with acetic acid, and again rendering alkaline, separates in colourless needles, and can be purified by distillation with steam; it melts at 110°, and dissolves readily in alcohol, benzene, and ether. Its alcoholic solution produces a green coloration with pine-wood moistened with hydrochloric acid. Like nicotyrine, it is a monacidic, tertiary base; the *picrate* melts at 124°, the *platinochloride* at 171°, the *mercurichloride* at 155°, and the *methiodide* at 196—197°.

Dihydronicotyrine (*1-methyl-2-pyridyldihydropyrroline*), resulting from the reduction of iodonicotyrine with zinc and hydrochloric acid, is a liquid boiling at 248° (corr.) which in all its properties greatly resembles nicotine; it is strongly alkaline, and behaves as a diacidic base. The *platinochloride*, $C_{10}H_{12}N_2,H_2PtCl_6$, has no definite melting point, the *picrate* melts at 156°; the methiodide does not crystallise, but the corresponding platinochloride, $C_{10}H_{12}N_2,Me_2PtCl_6$, melts at 240—242°. The base gives no colour reaction with the pine-wood, but decolorises permanganate in acid solution.

The authors have not succeeded in obtaining nicotyrine from nicotine. G. T. M.

Derivatives of 3′-Ethyllepidine (4′-Methyl-3′-ethylquinoline). By HENDRICK BYVANCK (*Ber.*, 1898, 31, 2143—2154).—(2 or 4)-*Amido-2′-hydroxy-4′-methyl-3′-ethylquinoline*, $NH_2\cdot C_6H_3 < \begin{matrix} CMe{:}CEt \\ N{=\!=}C\cdot OH \end{matrix}$, obtained by heating together metaphenylenediamine and ethylic ethylacetoacetate in sealed tubes at 165—170°, crystallises in fine, shining, colourless needles, and melts and decomposes at 277—284°; it is sparingly soluble in benzene and ether, but dissolves readily in ethylic and methylic alcohols, yielding solutions with a beautiful, blue fluorescence. It possesses both basic and acidic properties, dissolves readily in dilute sulphuric acid, and is reprecipitated by sodium carbonate. The *hydrochloride* crystallises in radiate groups of needles; the nitrate in hard prisms; and the *cadmiochloride* in bundles of long needles; the *zincochloride* and *mercurichloride* crystallise in brownish prisms. Ferric chloride produces a brown precipitate in solutions of the base.

(2 or 4)-2′-*Dihydroxy-4′-methyl-3′-ethylquinoline*,

$$OH\cdot C_6H_3 < \begin{matrix} CMe{:}CEt \\ N{=\!=}C\cdot OH \end{matrix},$$

is formed on heating a solution of diazohydroxyethyllepidine; its salts readily dissociate on treatment with water. It is insoluble in ether, slightly soluble in benzene and light petroleum, but dissolves readily in methylic and ethylic alcohols. It separates from chloroform, in which it is somewhat sparingly soluble, in white needles, and melts and decomposes at 263—273°.

2′-*Chloro*-(2 or 4)-*amido-4′-methyl-3′-ethylquinoline*,

$$NH_2\cdot C_6H_3 < \begin{matrix} CMe{:}CEt \\ N{=\!=}CCl \end{matrix},$$

is produced when the hydrochloride of amidohydroxyethyllepidine, heated with phosphorus oxytrichloride at 135—140° during $2\frac{1}{2}$—3 hours, is purified by precipitation with ammonia and crystallisation from light petroleum, when it forms slender, white needles and melts sharply at 138°. It dissolves readily in methylic and ethylic alcohols, giving solutions with a blue fluorescence, and is readily soluble in benzene. Its salts, with hydrochloric, nitric, and sulphuric acids, form solutions having a beautiful, green fluorescence. The *picrate* crystallises in plates, and the *chromate* is sparingly soluble; of its double salts, that with mercuric chloride forms prisms, whilst that with zinc chloride is obtained in oily drops which solidify to yellow flocks. The hydrochloride, when treated with gold chloride, gives a precipitate of metallic gold.

(2 or 4)-*Amido-4′-methyl-3′-ethylquinoline*, $NH_2\cdot C_6H_3 < \begin{matrix} CMe{:}CEt \\ N{=\!=}CH \end{matrix}$, is most readily prepared by heating amidochlorethyllepidine with hydriodic acid, potassium iodide, and phosphorus. The free base separates from ether, on the addition of light petroleum, in beautiful, colourless, prismatic crystals, melts at 84°, is readily soluble in alcohol, methylic alcohol, benzene, ether, and chloroform, less so in water, and sparingly in light petroleum. Its aqueous solution exhibits a blue fluorescence.

The *picrate* forms yellow flocks or fine yellow needles. The *hydriodide*, $C_{12}H_{14}N_2,HI$, decomposes at 260° and melts at 276°.

(2 or 4)-*Hydroxy-4′-methyl-3′ethylquinoline*, $OH \cdot C_6H_3 < \begin{matrix} CMe{:}CEt \\ N{=\!=}CH \end{matrix}$, obtained by the action of nitrous acid on the foregoing base, has phenolic properties, forms colourless crystals, and melts at 189°.

(2 or 4)-*Amido-4′-methyl-3′-ethylquinolinesulphonic acid*, formed by heating amidoethyllepidine with fuming sulphuric acid on the water bath, crystallises in beautiful, yellow needles which melt above 300°, and appear to be anhydrous; calcium acetate and barium chloride produce no precipitate in its solution. It may be oxidised by potassium permanganate, and the product has the properties of a strong acid, giving a *barium* salt which does not dissolve even in strong hydrochloric acid, and a greenish-blue *copper* salt; the latter, when decomposed with hydrogen sulphide, gives a *substance* which crystallises from water in white needles, and whose aqueous solution is coloured intensely yellow by ferric chloride.

4′-*Methyl-3′-ethylquinoline*, $C_6H_4 < \begin{matrix} CMe{:}CEt \\ N{=\!=}CH \end{matrix}$, is made from amidoethyllepidine by reducing its diazo-compound with stannous chloride and decomposing the hydrazine with copper sulphate. The *platinochloride*, $(C_{12}H_{13}N)_2,H_2PtCl_6$, crystallises in yellow, shining leaflets, and melts and decomposes at 196—200°; the *picrate* forms yellow needles and melts at 202°.

2′-*Chloro*-(2 or 4)-*hydroxy-4′-methyl-3′-ethylquinoline*,

$$OH \cdot C_6H_3 < \begin{matrix} CMe{:}CEt \\ N{=\!=}CCl \end{matrix},$$

prepared from amidochlorethyllepidine by the diazo-reaction, has marked acidic properties, and dissolves very sparingly in ether, but is more soluble in ethylic and methylic alcohols; it melts sharply at 227°; the *hydrochloride* forms long, reddish-yellow needles, and dissociates on addition of water. It is not reduced when heated with a mixture of hydriodic acid, potassium iodide, and amorphous phosphorus, but forms a *hydriodide* which is sparingly soluble in water. When oxidised with potassium permanganate, it yields 2-*chloro-4-methyl-3-ethylpyridine*-5 : 6-*dicarboxylic acid*, $\begin{matrix} CCl{=\!=}N{-}C \cdot COOEt \\ CEt \cdot CMe \cdot C \cdot COOEt \end{matrix}$, which forms beautiful, white crystals, and dissolves readily in water, alcohol, and ether; its aqueous solution gives a yellow coloration on the addition of ferrous sulphate, and a yellowish cloud with ferric chloride.

2′-*Iodolepidine*, $C_6H_4 < \begin{matrix} CMe{:}CH \\ N{=\!=}CI \end{matrix}$, may be obtained by heating the corresponding chlorolepidine with a mixture of hydriodic acid, potassium iodide, and amorphous phosphorus; it crystallises from light petroleum in long, colourless needles, melts at 90°, and dissolves readily in ether, methylic and ethylic alcohols, and light petroleum. Its *hydrochloride* and *hydriodide* crystallise in needles, and are sparingly soluble in water. It is easily reduced to lepidine by iron filings and sulphuric acid.

A. L.

Action of Methylic Iodide on Trimethyldihydroquinoline from Indole. Tetramethyldihydroquinoline. By ANTONIO PICCININI (*Gazzetta*, 1898, **28**, i, 187—196).—Zatti and Ferratini (Abstr., 1890, 1292) obtained a pentamethyldihydroquinoline by the action of methylic iodide on the trimethyldihydroquinoline recently examined by Ciamician and Piccinini (Abstr., 1897, i, 101); it is now shown that a tetramethyldihydroquinoline is formed in one stage of the reaction.

Tetramethyldihydroquinoline hydriodide, $C_{13}H_{17}N,HI$, is prepared by heating the trimethyldihydroquinoline with methylic iodide at 90° in an autoclave for 3 hours; the excess of methylic iodide is evaporated, and the tetramethyl-derivative separated from the tri- and pentamethyl derivatives by washing with acetic acid and treatment with alcohol. It forms lustrous, colourless scales melting at 227—228°, is stable when pure, and may be crystallised from water. On treatment with cold potash, it yields the *base*, which has the constitution

$$C_6H_4{<}\begin{matrix}CMe_2\cdot CH\\ \qquad\ \ \| \\ NMe\cdot CMe\end{matrix} \quad\text{or}\quad C_6H_4{<}\begin{matrix}CMe_2\cdot CMe\\ \qquad\ \ \| \\ NMe\cdot CH\end{matrix},$$

and is a highly refractive, colourless oil, boiling at 170—171° under 30 mm. pressure; under the ordinary pressure, it boils at 260°, with decomposition. The *picrate*, $C_{13}H_{17}N,C_6H_2(NO_2)_3\cdot OH$, crystallises in lustrous, yellow, laminæ melting at 107—108°.

Benzoyltetramethyldihydroquinoline, $C_{13}H_{16}N\cdot COPh$, is obtained by heating the base, suspended in potash, with benzoic chloride; it forms small, colourless, rhomb-shaped laminæ melting at 102°. *Benzoyltrimethyldihydroquinoline* crystallises in lustrous, yellow scales melting at 137—138°.

Tetramethyltetrahydroquinoline, $C_{13}H_{19}N$, obtained as an oil by reducing the dihydroquinoline with zinc and hydrochloric acid, does not redden on exposure to air; the *picrate*, $C_{13}H_{19}N,C_6H_2(NO_2)_3\cdot OH$, crystallises in small, yellow prisms melting at 148—149°. The *methiodide*, $C_{13}H_{19}N,MeI$, prepared by heating the base with methylic iodide at 100°, crystallises in colourless prisms, and volatilises at 240° without previously melting. On distilling tetramethyltetrahydroquinoline with hydriodic acid in a current of hydrogen, methylic iodide is eliminated, but the base formed was not obtained pure.

W. J. P.

Pyrazolecarboxylic Acids. By LUIGI BALBIANO (*Gazzetta*, 1898, **28**, i, 382—390).—Claisen (Abstr., 1897, i, 440) has synthesised 1-phenylpyrazole-4 : 5-dicarboxylic acid, $N{<}\begin{matrix}NPh\cdot C\cdot COOH\\ \qquad\ \ \| \\ CH-C\cdot COOH\end{matrix}$, which melts at 215—216° and gives a dimethylic salt melting at 75—76°. Balbiano and Severini (Abstr., 1893, i, 673) also prepared an acid to which they assigned this constitution, but the properties of which are different.

On repeating the previous work, the author finds that, on oxidising 1-phenylmethylethylpyrazole, 1-phenylpyrazole-3 : 4-dicarboxylic acid, melting at 234°, is obtained; its dimethylic salt crystallises in lustrous tablets melting at 97—98° (compare Abstr., 1893, i, 673). On

oxidising 1-phenyldimethylpyrazole as before, 1-phenyl-3-methylpyrazole-4-carboxylic acid is obtained; this crystallises in needles melting at 194—195°, and when heated gives 1-phenyl-3-methylpyrazole. From the mother liquors of its preparation, however, 1-phenyl-5-methylpyrazole-4-carboxylic acid, melting at 166—168°, was separated. The acid described by Balbiano and Severini as melting at 134° was a mixture of the two acids melting at 194—195° and at 166—168°; and the supposed 1-phenyl-3 : 4-dimethylpyrazole contained 1-phenyl-4 : 5-dimethylpyrazole. The erroneous constitution assigned by Balbiano and Severini was due to working with this mixture. W. J. P.

Aromatic Diurethanes of Piperazine. By Paul Cazeneuve and Moreau (*Compt. rend.*, 1898, **126**, 1802—1805).—*Orthochlorophenylic piperazinediurethane*, $C_6H_4Cl{\cdot}O{\cdot}CO{\cdot}N{<}{\substack{CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2}}{>}N{\cdot}COO{\cdot}C_6H_4Cl$, obtained by warming an alcoholic solution of piperazine and orthochlorophenylic carbonate in molecular proportion, forms small crystals melting at 165—172°. It is insoluble in water, slightly soluble in alcohol and ether, soluble in benzene and nitrobenzene, and very soluble in chloroform.

Thymylic piperazinediurethane,

$$C_6H_3MePr{\cdot}O{\cdot}CO{\cdot}N{<}{\substack{CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2}}{>}N{\cdot}COO{\cdot}C_6H_3MePr,$$

obtained in a similar manner from piperazine and thymylic carbonate, forms colourless crystals, melting at 139—140°; it is insoluble in water, slightly soluble in ether, and soluble in benzene and nitrobenzene. *Orthotolylic piperazinediurethane*,

$$C_6H_4Me{\cdot}O{\cdot}CO{\cdot}N{<}{\substack{CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2}}{>}N{\cdot}COO{\cdot}C_6H_4Me,$$

from piperazine and orthotolylic carbonate, forms crystals melting at 135° and is insoluble in water, soluble in alcohol, ether, and nitrobenzene, and very soluble in chloroform and benzene. The corresponding *meta-* and *para-*derivatives melt at 138—139° and 238° respectively, and resemble the ortho-compound in their behaviour with solvents. All these diurethanes, like those previously described, possess great stability, and are not altered by heating with alcoholic ammonia at temperatures below 200°; they are decomposed, however, by heating with concentrated potash at 100° and by ammonia above 200°. When heated with concentrated sulphuric acid, phenylic piperazinediurethane yields orthophenolsulphonic acid in theoretical amount, the remainder of the molecule being apparently completely destroyed. N. L.

Heptatomic Rings Containing Nitrogen: A Correction. By Emil Fischer (*Annalen*, 1898, **301**, 282—284).—The first compound containing nitrogen in a ring composed of seven atoms is ethylhydrocarbazostyril, $C_6H_4{<}{\substack{CH_2{\cdot}CH_2\\NEt{\cdot}NH}}{>}CO$, prepared by Fischer and Kuzel (Abstr., 1883, 1132). Rupe and Roesler (this vol., i, 573) are not justified, therefore, in ascribing the first member of this series to Busch (Abstr., 1895, i, 31). M. O. F.

The Cyclo-amides: 2′-Ketobenzomorpholine and 2′-Benzoparoxazine Derivatives. By HENRY L. WHEELER and BAYARD BARNES (*Amer. Chem. J.*, 1898, **20**, 555—568).—Whereas the sodium derivative of 2′-ketobenzomorpholine, $C_6H_4<\begin{smallmatrix}O-CH_2\\ NH\cdot CO\end{smallmatrix}$, gives rise, when treated with alkylic iodides, to derivatives of the type $C_6H_4<\begin{smallmatrix}O-CH_2\\ NR\cdot CO\end{smallmatrix}$, the silver salt, under similar conditions, produces substances of the type $C_6H_4<\begin{smallmatrix}O\cdot CH_2\\ N\colon C\cdot OR\end{smallmatrix}$, derived from 2′-hydroxybenzoparoxazine. This behaviour is analogous to that of the sodium and silver salts of the anilides; moreover, acidyl chlorides interact with the silver salt of 2′-ketobenzomorpholine in the same way as with the silver derivatives of the anilides (compare Wheeler and Walden, Abstr., 1897, i, 280), well characterised acyl derivatives being obtained, in which the acidyl group is united to nitrogen; it is noteworthy that Duparc (Abstr., 1887, 948) was unable to obtain an acetyl derivative by heating 2′-ketobenzomorpholine with acetic anhydride at 180°.

The substances of the type $C_6H_4<\begin{smallmatrix}O-CH_2\\ NR\cdot CO\end{smallmatrix}$, obtained from the sodium derivative of 2′-ketobenzomorpholine, are very stable, and are only partially decomposed by prolonged heating with concentrated hydrochloric acid, an ortho-alkylamidophenol, $OH\cdot C_6H_4\cdot NHR$, being formed. The derivatives of the type $C_6H_4<\begin{smallmatrix}O\cdot CH_2\\ N\colon C\cdot OR\end{smallmatrix}$ are, on the other hand, very unstable, 2′-ketobenzomorpholine being produced when they are exposed either to the action of the air or of cold dilute hydrochloric acid; in this, they resemble the isoanilides, and, like the latter, they readily interact with bases to form compounds of the type $C_6H_4<\begin{smallmatrix}O\cdot CH_2\\ N\colon C\cdot NHR\end{smallmatrix}$, which yield well-characterised salts.

Since, in general, the behaviour of 2′-ketobenzomorpholine is the same as that of formanilide, the normal structure, $C_6H_4<\begin{smallmatrix}O-CH_2\\ NH\cdot CO\end{smallmatrix}$, is given to it, instead of the enolic formula, $C_6H_4<\begin{smallmatrix}O-CH_2\\ N\colon C\cdot OH\end{smallmatrix}$. In discussing the structure of the amides, the authors point out that, as a rule, they cannot be looked on as possessing an enolic structure, for otherwise their hydroxy-derivatives would give rise, when heated, to imido-lactones, water being separated, as in the case of the hydroxy-acids; thus γ-hydroxyvaleramide, $OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot C(OH)\colon NH$, would produce the derivative $\begin{smallmatrix}CH_2-CH_2\\ CH_2\cdot O\cdot C\colon NH\end{smallmatrix}$, instead of decomposing with loss of ammonia, as is actually the case. Lachmann's view (Abstr., 1896, i, 601) that acetamide and benzamide contain a hydroxyl group, since they immediately generate hydrogen chloride when brought into contact with phosphorus pentachloride, whereas oxamethane, which undoubtedly contains a carbonyl group, does not do

so under the same conditions, is looked on as erroneous; the difference in behaviour probably depends simply on the amide chlorides produced in the former cases being far less stable, since they are of a more negative character, than that initially produced in the latter.

The *sodium* derivative, $C_6H_4<\begin{smallmatrix}O\cdot CH_2\\ \vert\\ N:C\cdot ONa\end{smallmatrix}$, of 2′-ketobenzomorpholine is best prepared by adding the latter (5 grams) to a solution of sodium in methylic alcohol, evaporating to dryness, and heating the residue during several hours at 100° under a pressure of 13 mm.; it is immediately decomposed by water, and, when heated with methylic iodide, gives rise to *1′-methyl-2′-ketobenzomorpholine*, $C_6H_4<\begin{smallmatrix}O\text{——}CH_2\\ \vert\\ NMe\cdot CO\end{smallmatrix}$. The latter is best prepared by dissolving 1·6 grams of sodium in a small quantity of methylic alcohol, and heating the solution with 2′-ketobenzomorpholine (10 grams) and methylic iodide (20 grams) for 7 hours at 135°; it crystallises from alcohol in large, colourless prisms, melts at 58—59°, boils at 156° under a pressure of 14 mm., and is insoluble in alkalis and in cold dilute hydrochloric acid; when heated with concentrated hydrochloric acid at 150—160° during several hours, it yields a small quantity of orthomethylamidophenol. *1′-Ethyl-2′-ketobenzomorpholine*, prepared in the same manner as the methyl derivative, is a pale yellow liquid which boils at 157—159° under a pressure of 15 mm.

The *silver* derivative of 2′-ketobenzomorpholine, prepared by dissolving the latter in alcohol and adding, first sodium ethoxide (1 mol.), and then the calculated amount of silver nitrate, is a light grey powder which is not affected by light or decomposed by water or alcohol. Phenol, however, immediately reduces it, silver being precipitated; similarly, the silver derivatives of formanilide and of 2 : 4-dichloroformanilide are decomposed by a solution of phenol in benzene, by aqueous quinol, or alcoholic β-naphthol.

2′-Methoxybenzoparoxazine, $C_6H_4<\begin{smallmatrix}O\cdot CH_2\\ \vert\\ N:C\cdot OMe\end{smallmatrix}$, prepared by heating the above described silver derivative with methylic iodide ($1\frac{1}{2}$ mols.) at 115—120° during 8 hours, is a colourless oil with a characteristic odour, which boils at 135—136° under a pressure of 21 mm., and is immediately decomposed by dilute hydrochloric acid, 2′-ketobenzomorpholine being regenerated. *2′-Ethoxybenzoparoxazine* boils at 135—136° under a pressure of 16 mm., whilst the corresponding *2′-isopropyl* derivative boils at 137—138° under a pressure of 14 mm., the *2′-isobutyl* derivative at 160—164° under a pressure of 21 mm., and the *2′-isoamyl* derivative at 174—175° under the same pressure.

The *1′-acetyl* derivative, $C_6H_4<\begin{smallmatrix}O\text{——}CH_2\\ \vert\\ NAc\cdot CO\end{smallmatrix}$, of 2′-ketobenzomorpholine, prepared by adding the calculated quantity of acetic chloride to the silver derivative suspended in ether, separates in long, white needles, melts at 77°, and can be recrystallised without change from water. The corresponding *benzoyl* derivative crystallises from benzene in colourless prisms, and melts at 93°.

2'-Anilidobenzoparoxazine, $C_6H_4<\begin{matrix}O\cdot CH_2 \\ N:\overset{|}{C}\cdot NHPh\end{matrix}$, prepared by the action of aniline on 2'-ethoxybenzoparoxazine, crystallises in colourless prisms, and melts at 126°; the *hydrochloride* melts at 220—223°, the *hydriodide* at 195—196°, and the *nitrate* at 147°. *2'-Metachloranilidobenzoparoxazine* crystallises from benzene in colourless plates, and melts at 112—114°; the *hydrochloride*, $C_{14}H_{10}N_2OCl,HCl$, melts and decomposes at 205—207°. The corresponding *β-naphthylamine* derivative, $C_{18}H_{14}N_2O$, crystallises from benzene in white leaflets, and melts at 154—155°; the *isobutylamine* derivative yields a *hydrochloride*, $C_{12}H_{16}N_2O,HCl$, which melts at 220—223°. *2'-Allylamidobenzoparoxazine* crystallises from light petroleum containing benzene, in colourless prisms, and melts at 63°; its *hydrochloride*, $C_{11}H_{12}N_2O,HCl$, crystallises in colourless needles, and melts at 190°.

W. A. D.

Preparation of Alloxanphenylhydrazone from Barbituric Acid. By OTTO KÜHLING (*Ber.*, 1898, **31**, 1972—1977. Compare Abstr., 1892, 442).—Alloxanphenylhydrazone is readily formed by the action of diazobenzene chloride solution on barbituric acid, the product being in every respect identical with that previously obtained by the action of phenylhydrazine on alloxan in acid solution. When the hydrazone is reduced with tin and hydrochloric acid, it yields uramil and aniline. *Alloxanorthonitrophenylhydrazone*,

$$NO_2\cdot C_6H_4\cdot NH\cdot N:C<\begin{matrix}CO\cdot NH \\ CO\cdot NH\end{matrix}>CO,$$

prepared from barbituric acid by the action of the diazo-chloride derived from orthonitraniline, crystallises in yellow, microscopic needles melting above 310°, has the properties of a feeble acid, and is reduced by tin and hydrochloric acid in the same way as alloxanphenylhydrazone. When boiled with sodium carbonate solution, it is converted into an unstable *substance*, which crystallises in pale yellow, slender needles, melts at 194—196°, and probably has the constitution, $NO_2\cdot C_6H_4\cdot NH\cdot N:CH\cdot CO\cdot NH\cdot COOH$. *Alloxanparanitrophenylhydrazone* forms lustrous, microscopic crystals, melts above 300°, and is converted by sodium carbonate into an unstable, yellow compound of the formula, $C_9N_4H_8O_5$, which melts at 193—194°.

A. H.

Action of Ethylic Chlorofumarate on Amidoximes. By C. WOLF (*Ber.*, 1898, **31**, 2110—2112).—When ethylic chlorofumarate is added to an alcoholic solution containing sodium ethoxide and the amide of benzhydroximic acid, benzenylamidoxime, dibenzenylazoxime, and the *sodium* derivative of a *compound* having the formula $C_{13}H_{12}N_2O_4$ are produced. The compound obtained by decomposing the sodium derivative with acids, crystallises from alcohol in lustrous, silky needles, and melts at 154°. It may have either of the following formulæ, $\begin{matrix}CPh:N—O \\ \overset{|}{N}H\cdot CO\cdot CH\end{matrix}>C\cdot COOEt$ or $\begin{matrix}CPh:N\cdot O \\ \overset{|}{N}H—CO\end{matrix}>C\cdot CH\cdot COOEt$. This substance does not yield an additive product with bromine, and its alcoholic solution gives no colour reaction with ferric chloride. The *silver* derivative, $C_{13}H_{11}N_2O_4Ag$, formed by treating its ammoniacal

solution with silver nitrate, melts at 94°, and yields a *methyl* derivative when heated at 100° with an alcoholic solution of methylic iodide. When hydrolysed, the compound, $C_{13}H_{12}N_2O_4$, yields *benzenylamidofumaric-esoanhydridecarboxylic acid*; this is sparingly soluble in the usual solvents, but dissolves readily in dilute alkalis; its alkaline solution decolorises potassium permanganate, and with silver nitrate it forms a silver salt.

Phenylethenylamidoxime and ethylic chlorofumarate give rise to *ethylic phenylethenylamidoximefumaric-esoanhydridecarboxylate*, which melts at 158°, and may have a constitution corresponding with either

$$\begin{array}{l} CH_2Ph\cdot C\colon N\text{——}O \\ \quad\quad\;\; | \\ \quad\quad NH\cdot CO\cdot CH \end{array}\!\!>\!C\cdot COOEt \text{ or } \begin{array}{l} CH_2Ph\cdot C\colon N\cdot O \\ \quad\quad\;\; | \\ \quad\quad NH\cdot CO \end{array}\!\!>\!C\colon CH\cdot COOEt.$$

G. T. M.

Action of Primary Amines on Dinitrosacyls. By J. Boeseken (*Rec. Trav. Chim.*, 1897, **16**, 297—353. Compare Holleman, Abstr., 1893, 205).—When a primary amine reacts with a glyoxime peroxide (dinitrosacyl), $\begin{array}{l} R\cdot CO\cdot C\colon N\cdot O \\ \quad\quad\;\;\, | \quad\quad\; | \\ R\cdot CO\cdot C\colon N\cdot O \end{array}$, one of the acidyl groups is removed as a substituted amide, $R\cdot CO\cdot NHR_1$, whilst the residue combines with a second molecule of the amine, yielding a brown, crystalline product, $R\cdot CO\cdot C\!\ll\!\begin{array}{l} N\text{—}O \\ CH\colon N \end{array}\!\!>\!NR_1$, which the author terms an *isotriazoxole*. When the brown compound is gently heated, it is converted into an isomeric, colourless compound, a *triazoxole*, $R\cdot CO\cdot C\!\ll\!\begin{array}{l} O\cdot NR_1 \\ N\cdot CH \end{array}\!\!\gg\!N$.

Glyoxime peroxides form condensation products with primary amines only; with pyridine, methylaniline, and di-isobutylamine no reaction takes place. Acid groups also appear to interfere with the reaction; sulphanilic acid, metanitraniline, and carbamide do not react with glyoxime peroxides; paramidophenol, or one of the naphthylamines, yields amorphous products. A group in the ortho-position relatively to the amido-group of aniline sensibly retards the reaction; for example, metaxylidene acts very slowly and also incompletely. The reaction takes place more energetically the stronger the base used, thus benzylamine reacts more readily than phenylhydrazine, and the latter than aniline.

The isotriazoxoles are unstable compounds, and attempts to prepare benzoyl or acetyl derivatives proved fruitless. The triazoxoles are more stable, and are characterised by their insolubility in most solvents.

When dibenzoylglyoxime peroxide (5 grams) is boiled for 2 hours with a mixture of aniline (5 grams) and ether (25 grams), benzanilide is deposited, and the oil left after distilling off the ether yields, on the addition of acetic acid, *benzoylphenylisotriazoxole*,

$$CBz\!\ll\!\begin{array}{l} CH\colon N \\ N\text{—}O \end{array}\!\!>\!NPh,$$

in the form of crystalline needles melting at 97°. The primary product of the action of aniline on dibenzoylglyoxime peroxide is not the brown, crystalline compound, but a substance which could not be obtained in a pure form; it is readily soluble in alkalis, and the alkaline solu-

tion has many of the properties of amidoximes, and after a time yields a resin.

Benzoylparatolylisotriazoxole, $C_{16}H_{33}N_3O_2$, crystallises in long, glistening needles, which cannot be recrystallised without undergoing decomposition.

Benzoylanilidoisotriazoxole, $CBz{<}{\overset{CH:N}{\underset{N—O}{}}}{>}N{\cdot}NHPh$, obtained from dibenzoylglyoxime peroxide and phenylhydrazine, crystallises on the addition of acetic acid as the *acetate* in red needles; these detonate at 75°, and on exposure to the air lose acetic acid, and become transformed into a yellow powder, the isotriazoxole, which crystallises from methylic alcohol in small, clear yellow needles, decomposing at 65°.

Benzoylbenzylisotriazoxole, crystallising in green needles and decomposing at 112°, and *benzoylbenzylamide*, melting at 106°, are obtained by the action of benzylamine on glyoxime peroxide in ethereal solution. *Benzoylisobutylisotriazoxole* crystallises in green needles. Benzoylisotriazoxole and benzoylethylisotriazoxole could not be obtained in a crystalline form.

Paratoluoylphenylisotriazoxole, $C_6H_4Me{\cdot}CO{\cdot}C{<}{\overset{CH:N}{\underset{N—O}{}}}{>}NPh$, obtained by boiling an ethereal solution of aniline with diparatoluoylglyoxime peroxide, forms brown crystals. *Paratoluoylparatolylisotriazoxole*, decomposing at 125°, and *paratoluoylparatoluidide*, melting at 165°, are obtained from paratoluidine and diparatoluoylglyoxime peroxide. The first products formed are paratoluoylparatoluidide and an *oxime*, $C_6H_4Me{\cdot}CO{\cdot}C(:N{\cdot}OH){\cdot}CH:N{\cdot}N(OH){\cdot}C_6H_4Me$, which can be extracted from the ethereal solution by alkalis; it forms small, colourless crystals readily soluble in ether, acetone, or alcohol, and has many of the properties of an amidoxime; it is readily converted by the loss of water, even on treatment with the usual solvents, into paratoluoylparatolylisotriazoxole. A small quantity of *paratoluoylmetaxylylisotriazoxole* is obtained by the action of metaxylidine on paratoluoylglyoxime peroxide. *Paratoluoylbenzylisotriazoxole*, decomposing at 115°, and *paratoluoylbenzylamide*, melting at 133°, are obtained from benzylamine, and the same glyoxime peroxide. *Paratoluoylanilidoisotriazoxole*, crystallising from a mixture of ether and methylic alcohol in yellow needles, and *paratoluoylphenylhydrazide*, melting at 167°, are obtained from phenylhydrazine and diparatolyldinitrosacyl. *Paranisoylparatolylisotriazoxole*,

$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}C{<}{\overset{CH:N}{\underset{N—O}{}}}{>}N{\cdot}C_6H_4Me,$$

crystallises in brilliant, brown needles; *paranisoylbenzylisotriazoxole* crystallises in long, green needles decomposing at 117°, and *paranisoylbenzylamide* crystallises in colourless needles melting at 126°. *Paranisoylanilidoisotriazoxole* crystallises from a mixture of ether and methylic alcohol in small needles decomposing at 97°; it forms red salts with acetic and hydrochloric acids, but they are unstable. *Paranisoylphenylhydrazide* melts at 179°.

When paratoluoylparatolylisotriazoxole is reduced with stannous chloride and acetic acid, the products are a small quantity of the

isomeric triazoxole, ammonia, methylamine, paratoluidine, and paratoluic acid; with zinc and acetic acid, a much larger quantity of the isomeride is formed, and the same products as when using stannous chloride. With an alkaline solution of stannous chloride, the products are ammonia, paratoluidine, paratoluic acid, the unaltered substance, and a small quantity of oxalic acid. When warmed with an alcoholic solution of sodium methoxide or ethoxide, the isotriazoxole unites with methylic or ethylic alcohol, yielding methylic or ethylic derivatives of the oxime derivative described above; the *methylic* derivative, $C_6H_4Me\cdot CO\cdot C(:N\cdot OH)\cdot CH:N\cdot N(OMe)\cdot C_6H_4Me$, forms small crystals soluble in ether, but insoluble in light petroleum.

Isotriazoxoles are converted into their colourless isomerides by boiling with acetic chloride, and when boiled with acetic anhydride and dry sodium acetate are completely decomposed, for example, isotriazoxole yields oxalic and paratoluic acids, ammonia, and acetoparatoluidide. Oxalic and paratoluic acids are also obtained by oxidising the triazoxole with alkaline potassium permanganate.

When boiled with concentrated potassium hydroxide, paratoluoylparatolylisotriazoxole yields a compound in the form of orange-red crystals melting at 188°, and another which is identical with the oxime derivative, $C_{17}H_{17}N_3O_3$, described above. When the isotriazoxoles are heated to 100°, they decompose with detonation; at 50°, no transformation takes place, and even when heated at 60—70° for 12 hours but little of the colourless isomeric triazoxoles are formed. The transformation takes place much more readily in solution, for example, in alcohol, acetic chloride, or glacial acetic acid. Acetic chloride especially appears to facilitate the transformation.

Paratoluoylphenyltriazoxole, $C_6H_4Me\cdot CO\cdot C{\lessgtr}^{O\cdot NPh}_{N-CH}{\gtrless}N$, obtained by boiling the corresponding isotriazoxole with an excess of alcohol (97 per cent.) until the mass becomes colourless, crystallises from glacial acetic acid and melts at 211°.

Paratoluoylparatolyltriazoxole melts at 208°.

Paratoluoyltriazoxole, obtained by heating diparatolylglyoxime peroxide with concentrated alcoholic ammonia, melts at 165°.

Paranisoyltriazoxole, $C_{10}H_9N_3O_3$, obtained by heating diparanisoylglyoxime peroxide for 2 hours in sealed tubes with alcoholic ammonia, crystallises from alcohol in colourless needles melting at 144°. *Paranisoylbenzyltriazoxole*, obtained from the iso-compound by boiling with glacial acetic acid, crystallises in needles melting at 190°.

Paratoluoylparatolyltriazoxole is not altered either by boiling with stannous chloride in acid solution, or by zinc dust and acetic acid. When heated with acetic anhydride and anhydrous sodium acetate, it is decomposed, yielding ammonia together with oxalic and paratoluic acids. Paratoluoyltriazoxole, when heated with acetic anhydride and sodium acetate, yields an *acetyl* derivative, $C_{12}H_{11}N_3O_3$, melting above 260°. When heated at 180° with concentrated hydrochloric acid, the triazoxole is completely decomposed into carbonic anhydride, ammonia, paratoluic acid and paratoluidine; it is not decomposed when boiled with potassium permanganate unless the boiling is continued for 24 hours, when an acid, probably terephthalic, is formed.

Paratolyltriazoxole, $N{<}\genfrac{}{}{0pt}{}{CH\cdot O}{CH:N}{>}N\cdot C_6H_4Me$, is obtained as its *potassium* salt when paratoluoylparatolyltriazoxole is gently heated with about ten times its weight of concentrated potassium hydroxide until it is completely dissolved; it is separated from the potassium paratoluate, which is also formed, by digestion with alcohol; the free paratolyltriazoxole cannot be recrystallised, as it undergoes decomposition. It is readily soluble in alcohol, acetone, or ether, sparingly in acetic acid, and melts and decomposes at 138°. Paratolyltriazoxole, when boiled with dilute acetic or dilute hydrochloric acid, is decomposed into carbonic anhydride, paratoluidine, and cyanamide, according to the equation $C_9H_9N_3O + H_2O = C_7H_7NH_2 + CO_2 + CN_2H_2$.

Phenyltriazoxole, $CH{<}\genfrac{}{}{0pt}{}{N—CH}{O\cdot NPh}{>}N$, obtained in the form of its *potassium* salt by boiling paratoluoylphenyltriazoxole with potassium hydroxide, melts at 110—120°. The potassium salt is unstable and decomposes when recrystallised; its *ammonio-silver* salt, $C_8H_6N_3OAg + NH_3$, crystallises well, and when heated at 70° evolves ammonia and yields the *silver* salt, $C_8H_6N_3OAg$. Phenyltriazoxole is readily decomposed into carbonic anhydride, aniline, and cyanamide, boiling with water being sufficient to bring about the decomposition.

J. J. S.

Alloxuric Bases Present in Urine. By MARTIN KRÜGER and GEORG SALOMON (*Zeit. physiol. Chem.*, 1898, **24**, 364—394).—The investigation of the xanthine and hypoxanthine fractions of the alloxuric bases obtained from 10,000 litres of human urine (Abstr., 1896, ii, 200) is described. The former, consisting of 22·2 grams, and not 13 grams as formerly stated, was found to contain 11·36 grams of heteroxanthine, 1·3 grams of paraxanthine, 3·88 grams of xanthine, and 5·14 grams of a new methylxanthine. Paraxanthine is separated from its congeners by extracting with water in which it is easily soluble, whilst heteroxanthine is easily isolated by means of its sparingly soluble sodium derivative; a separation, however, of xanthine from the new methylxanthine could not be effected in this fraction.

The *platinochloride*, $(C_7H_8N_4O_2)_2,H_2PtCl_6 + H_2O$, of paraxanthine separates from water in orange crystals belonging to the anorthic system; $a:b:c = 0·8066:1:1·30098$; $\alpha = 80°\ 30'$; $\beta = 88°\ 13'$; $\gamma = 94°\ 27'$ (Arzruni).

The hypoxanthine fraction contained xanthine, hypoxanthine, adenine, epiguanine, and the new *methylxanthine*, $C_6H_6N_4O_2$; 2·5 grams of the latter was isolated in a pure state, but it was found impossible to separate the remainder from xanthine. It is obtained from water as a colourless, dull, crystalline powder, and is easily soluble in ammonia, caustic soda, and dilute mineral acids; its *aurochloride* cystallises in lustrous plates, and its *platinochloride* in stellar aggregates of needles. The new substance gives Fischer's xanthine reaction (*Ber.*, 1897, 2236, note), and, with silver nitrate, yields a well-defined *additive* compound which cannot be distinguished in appearance or solubility from that obtained from xanthine; the new base is, by

exclusion, probably a 1-*methylxanthine* (compare Fischer and Ach, following abstract).

The bases of the hypoxanthine fraction were separated by taking advantage of the difference in the solubilities of their lead derivatives; xanthine, and 1-methylxanthine were precipitated by basic lead acetate, whilst from the filtrate 1-methylxanthine (free from xanthine), hypoxanthine, and a small quantity of adenine were thrown down on adding ammoniacal lead acetate. The remainder of the adenine and the whole of the epiguanine were obtained from the second filtrate by the addition of an ammoniacal solution of silver. The adenine was characterised by its hydrochloride, sulphate, and picrate; the last two salts were analysed; the picrate is anhydrous, and does not contain $1H_2O$ as stated by Bruhns (Abstr., 1890, 534). Hypoxanthine was characterised by its hydrochloride and picrate, both of which were analysed; whilst epiguanine was recognised only by qualitative tests.

W. A. D.

Further Syntheses of Xanthine Derivatives from Methylated Uric Acids. By EMIL FISCHER and FRIEDRICH ACH (*Ber.*, 1898, 31, 1980—1988. Compare Abstr., 1897, i, 641).—Only those methyl derivatives of uric acid which contain two methyl groups in the alloxan nucleus are converted by treatment with the chlorides of phosphorus into xanthine derivatives, uric acid itself, and such of its methyl derivatives as have not this constitution, being thereby converted into purine derivatives. When, however, these methyluric acids are treated with phosphorus oxychloride alone, they yield xanthine derivatives.

8-*Chloro-3-methylxanthine*, $\begin{matrix} NH\cdot CO-C\cdot NH \\ | \qquad\quad \| \\ CO\cdot NMe\cdot C-N \end{matrix}\!\!>\!CCl$, is formed when 3-methyluric acid (α-methyluric acid) is heated with phosphorus oxychloride, and the product, after the removal of the excess of oxychloride, treated with alcohol. It crystallises in lustrous, flat prisms containing $1H_2O$, and decomposes and froths up at 340—345°. The *sodium*, *ammonium*, and *barium* derivatives all crystallise in slender needles, whilst the *silver* derivative is a gelatinous precipitate which is not decomposed by boiling water. 8:3-Chloromethylxanthine is readily converted by methylation, by means of methylic iodide or potassium methyl sulphate, into *chlorotheobromine*, $C_7H_7N_4O_2Cl$, which crystallises in short, lustrous prisms or fascicular groups of needles melting at 304° (corr.). It dissolves in about 250 parts of boiling water and forms crystalline *sodium*, *ammonium*, and *barium* derivatives. It is almost quantitatively converted into theobromine by hydriodic acid, whilst on treatment with methylic iodide and caustic potash, it yields caffeine. The compound obtained from chloromethylxanthine is identical with that prepared directly from theobromine by the action of chlorine or chloride of iodine. The formation of theobromine from α-uric acid shows that the latter is a 3-methyluric acid, since it is known to contain the methyl group in the alloxan nucleus.

3-*Methylxanthine*, $\begin{matrix} NH\cdot CO-C\cdot NH \\ | \qquad\quad \| \\ CO\cdot NMe\cdot C-N \end{matrix}\!\!>\!CH$, obtained by the reduction of chloromethylxanthine with hydriodic acid and phosphonium

iodide, crystallises in slender, lustrous needles, which gradually decompose above 360° without melting. It dissolves readily in alkalis, and yields crystalline salts. It also yields salts with acids; the *hydrochloride* crystallises in slender needles, the *hydriodide* in compact prisms, and the *nitrate* also forms compact crystals. It yields a crystalline precipitate with silver nitrate, whereas ammoniacal silver oxide produces a white, amorphous precipitate; like all xanthine derivatives, it gives the murexide reaction. This compound is quite distinct from the methylxanthine found by Krüger and Salomon (preceding abstract) in urine. 3-Methylxanthine is converted by methylation into theobromine or caffeine according to the amount of methylic iodide employed.

3:7-Dimethyluric acid is directly converted into chlorotheobromine by treatment with phosphorus oxychloride, a yield of 90 per cent. of the theoretical being obtained.

In addition to the four monomethyluric acids of known constitution, a fifth, termed δ-uric acid, has also been described and must, according to the authors, be regarded as a chemical individual. The formula at present accepted for uric acid does not admit of the existence of five isomerides of this methyl derivative, and it seems probable that the isomerism may be of a geometrical character. A. H.

Bromine Derivatives of Morphine. By HENRI CAUSSE (*Compt. rend.*, 1898, **126**, 1799—1802).—*α-Tetrabromomorphine hydrobromide*, obtained by the action of bromine on morphine in presence of concentrated hydrobromic acid, forms colourless crystals melting at 218°. Its molecular weight, determined cryoscopically, was found to be 678 (theory, 682). It is insoluble in cold water, methylic alcohol, and chloroform, but fairly soluble in boiling water and ethylic alcohol; the solutions are optically active. Sodium ethoxide and silver oxide remove part of the bromine, and a *substance* is formed which crystallises in yellow needles and has the properties of a quinone. When boiled with soda, it blackens, and an alkaline gas having the odour of methylamine is evolved; the residue, when acidified and extracted with ether, yields phenol. *β-Tetrabromomorphine hydrobromide* is obtained by adding bromine to a solution of morphine in chloroform, ether, or water, and subsequently digesting the product with dilute sodium thiosulphate solution, and also by cautiously adding hydrogen peroxide or potassium permanganate to the liquid from which the isomeric α-compound has crystallised. It forms infusible yellow, crystals, insoluble in cold water, but soluble in all proportions in methylic alcohol, ethylic alcohol, and acetone. Silver oxide removes the whole of the bromine, with formation of an amorphous, brown *substance*. When treated with boiling soda, it is completely destroyed and yields traces of phenol. *Tetrabromomorphine*, $C_{17}H_{15}Br_4NO_3 + 2H_2O$, is obtained by precipitating the aqueous solution of the α-hydrobromide with sodium carbonate and recrystallising the precipitate from alcohol. It is difficult to obtain perfectly colourless, and is usually of a blue or violet tint. It has both acid and basic functions. The *sulphate* and the *oxalate* of tetrabromomorphine are colourless, crystalline salts, insoluble in water, alcohol, and ether. When baryta water, or an

ammoniacal solution of barium chloride, is added to an aqueous solution of α-tetrabromomorphine hydrobromide, a *compound* of the formula $C_{17}H_{15}Br_4NO_3,\frac{1}{2}BaO + H_2O$ is produced. It forms small, colourless crystals, insoluble in water, but soluble in alcohol and acetone. *Tribromomorphine hydrobromide* is contained in the mother liquor obtained in the preparation of α-tetrabromomorphine hydrobromide; it forms crystals, melting at 178°, which are difficult to obtain free from colour. When treated with baryta water, an amorphous, green powder of variable composition is produced. N. L.

Electrolytic Preparation of Hydrocotarnine. By ERICH BANDOW and RICHARD WOLFFENSTEIN (*Ber.*, 1898, **31**, 1577—1578).—Cotarnine, $C_{12}H_{15}NO_4$ (30 grams), is dissolved in dilute sulphuric acid (1 : 5; 170 grams), and the solution is electrolysed until, after some 4 hours, it has become colourless, and with ammonia, a sample gives a pure white precipitate having the melting point of hydrocotarnine, $C_{12}H_{15}NO_3$. The electrodes are of platinum foil, the anode being immersed in dilute sulphuric acid; the current density at the cathode is about 3·5 ampères, and the E.M.F. about 5·3 volts. Crude cotarnine may be used, as obtained from the mother liquor after narcotine has been treated with manganese dioxide and sulphuric acid and the opianic acid has been separated; even in this case, the hydrocotarnine obtained is pure.

Hydrastinine, $C_{11}H_{13}NO_3$, may be converted into hydrohydrastinine, $C_{11}H_{13}NO_2$, in a similar manner. C. F. B.

Condensation of Aldehydes with Hydrocotarnine. By JULIUS KERSTEN (*Ber.*, 1898, **31**, 2098—2103. Compare Abstr., 1896, i, 264).—As hydrocotarnine is not acted on by fuming hydrochloric acid at ordinary temperatures, the agent may accordingly be employed in effecting condensations between this base and various aldehydes. Isonarcotine is obtained by mixing together the above base and opianic acid, in molecular proportion, in the presence of fuming hydrochloric acid, and warming the mixture for some time at 60—70°.

Under similar conditions, combination takes place between metanitrobenzaldehyde and hydrocotarnine, in molecular proportion, unaccompanied by the elimination of water. The *compound*,

$$NO_2\cdot C_6H_4\cdot CH(OH)\cdot C_{12}H_{14}NO_3,$$

melts at 170—171°, is soluble in alcohol, benzene, and chloroform, but insoluble in ether, petroleum, and solutions of the alkalis and alkali carbonates, and forms a green solution with concentrated sulphuric acid. The *platinochloride* and the *aurochloride* are insoluble, the former being yellow, and the latter brown. The salts of the base with halogen acids are soluble in water.

Combination occurs between 2 molecules of salicylaldehyde and 1 of the base without elimination of water, the *compound* produced being insoluble in ether, benzene, chloroform, petroleum, and alkaline solutions, but soluble in alcohol and salicylaldehyde; its *platinochloride* is a red, flocculent precipitate.

Benzaldehyde and hydrocotarnine, in the presence of hydrochloric acid, condense to form the *base*, $C_6H_5\cdot CH(C_{12}H_{14}NO_3)_2$, water being eliminated (Abstr., 1896, i, 711). The condensation product crys-

tallises from dilute alcohol in white needles melting at 229—230°, and is soluble in benzene, chloroform, and benzaldehyde, but insoluble in ether, petroleum, and alkaline solutions. The *platinochloride*, $(C_{31}H_{34}N_2O_6),H_2PtCl_6$, is obtained in yellow flakes. Piperonal behaves in a similar manner to benzaldehyde; the *base* formed,

$$CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH(C_{12}H_{14}NO_3)_2,$$

melts at 202°, and yields an insoluble, yellow *platinochloride*.

Cinnamaldehyde also combines with 2 molecular proportions of hydrocotarnine, but no elimination of water occurs in the presence of strong hydrochloric acid; the *base* thus produced melts and decomposes at 228—230°, and yields an insoluble, yellow *platinochloride*. When 73 per cent. sulphuric acid is employed instead of hydrochloric acid, the condensation of 2 molecules of hydrocotarnine and 1 of the aldehyde is accompanied by elimination of water; the compound thus obtained, $CHPh{:}CH\cdot CH(C_{12}H_{14}NO_3)_2$, melts at 139—140°, and yields a *platinochloride*, $(C_{33}H_{36}N_2O_6),H_2PtCl_6$.

The above condensation products, when dissolved in strong sulphuric acid, exhibit distinctive colorations. G. T. M.

Strychnine. By Julius Tafel (*Annalen*, 1898, **301**, 285—348. Compare Abstr., 1892, 1012).—When a current of 5 ampères at a potential of 3·5 volts, is passed through a solution of 30 grams of strychnine in 180 grams of concentrated sulphuric acid mixed with 120 grams of water, two poisonous bases, strychnidine and tetrahydrostrychnine, are produced. After 10 hours treatment, the colourless liquid is diluted with 4 times its own volume of water, nearly neutralised with barium carbonate, and, after filtration, treated with a slight excess of baryta, which precipitates strychnidine and barium sulphate.

Strychnidine, $C_{20}H_{22}NO{<}^{CH_2}_{\underset{N}{|}}$, crystallises from alcohol in stellate aggregates of colourless needles, and sinters at 246° (uncorr.), melting to a brown liquid at 250·5°; in a vacuum, it melts at 252°, forming a colourless solution. Impure specimens of the base crystallise in thin, reddish needles melting at 246—248°. Strychnidine boils at 290—295° under a pressure of 14 mm., the colourless distillate immediately becoming crystalline; it dissolves very sparingly in water, forming a distinctly alkaline solution. The base requires 32 parts of boiling absolute alcohol for dissolution, 120 parts of the solvent being necessary at 20°; it dissolves in 50 parts of boiling 60 per cent. alcohol, and in 14 parts of boiling benzene. Chloroform dissolves it still more readily, and when the solution in 10 parts of this medium is treated with 20 parts of ether, 70 per cent. of the base crystallises in prisms. A 6·4 per cent. solution of the base in chloroform has the specific rotatory power $[\alpha]_D = -8·28°$ at 20°. A solution of strychnidine in concentrated sulphuric acid gives coloration with oxidising agents, but aqueous solutions of its salts, in presence of excess of acid, become intensely red with potassium dichromate, hydrogen peroxide, ferric chloride, or sodium nitrite; concentrated nitric acid produces the same effect when added to the base. In this respect,

it resembles dimethylstrychnine, methylisostrychnic acid (*loc. cit.*), and methyltetrahydroquinoline (kairoline); the highly sensitive character of the ferric chloride reaction is also peculiar to these four compounds. Dimethylaniline, dissolved in hydrochloric acid, gives a yellow coloration with ferric chloride, but the test is less sensitive than in the case of kairoline and strychnidine. When bromine water is added to an acid solution of strychnidine, a pink coloration is developed, gradually deepening to violet-red; on continuing the addition of bromine, a dirty violet solid is precipitated, whilst the liquid becomes colourless. Diazobenzene chloride, when added to an acetic acid solution of strychnidine, produces a yellow azo-compound which forms a magenta-coloured solution in dilute hydrochloric acid. On heating the base with benzaldehyde and zinc chloride, a yellow product is obtained, which, when extracted with water and dissolved in alcohol, gives an intense, malachite-green coloration with ferric chloride. An intense red liquid is obtained on adding sodium nitrite to a concentrated solution of strychnidine in excess of hydrochloric acid, but it rapidly becomes brownish-yellow, and deposits a yellow, micro-crystalline precipitate. Ten per cent. nitric acid decomposes the base when boiled with it, yielding a deep red solution which finally becomes olive green; whilst acetic anhydride and phosphorus pentachloride give rise to indefinite products. Strychnidine has the disagreeable, bitter taste of strychnine and deoxystrychnine; it also resembles these alkaloids in its poisonous properties. Unlike deoxystrychnine, it yields two series of salts, of which those containing one molecular proportion of acid are neutral towards litmus, whilst the others have an acidic action, and readily part with a portion of the combined acid. The *hydrochloride*,

$$C_{21}H_{24}N_2O,HCl,$$

forms slender, colourless needles, and when treated with mercuric chloride yields a gelatinous precipitate which becomes crystalline on boiling; potassium dichromate precipitates slender, pale yellow needles, and develops an intense red coloration in presence of excess of acid. The *dihydrochloride*, $C_{21}H_{24}N_2O,2HCl$, crystallises in colourless needles, and is converted into the hydrochloride on crystallisation from water. The *methiodide*, $C_{21}H_{24}N_2O,MeI + 2H_2O$, crystallises from water in aggregates of needles several mm. in length.

Tetrahydrostrychnine, $C_{20}H_{22}NO(NH)\cdot CH_2\cdot OH$, crystallises from alcohol in colourless prisms containing one molecular proportion of the solvent, which it retains in a vacuum, but loses completely at 100°, it then melts at 202° to a colourless liquid; the base dissolves in 280 parts of water at 20°, and the solution is strongly alkaline towards phenolphthalein, litmus, and turmeric. Tetrahydrostrychnine dissolves in about 20 parts of boiling alcohol or of boiling benzene, and in 14 parts of boiling 95 per cent. alcohol; it dissolves very readily in chloroform, and is precipitated in microscopic needles on adding ether to this solution. The base resembles strychnidine in its behaviour towards concentrated sulphuric acid and potassium dichromate, but yields a wine-red solution when the hydrochloride is treated with ferric chloride or chromic acid, the latter producing a reddish-brown precipitate in concentrated solutions; sodium nitrite has no action on dilute solutions, and precipitates the hydrochloride of the nitrosamine

from concentrated solutions. Bromine water develops a violet or wine-red coloration in a solution of the hydrochloride, and concentrated nitric acid forms an intense yellow solution, which gradually becomes deep red. Acetic anhydride converts the base into a crystalline acetyl derivative, which, when dissolved in concentrated sulphuric acid and treated with potassium dichromate, develops a beautiful violet coloration. On heating the base with concentrated hydrochloric acid at 100° during 3 hours, or with phosphorus oxychloride, it is resolved into strychnidine, which is also formed in association with iodo-bases when tetrahydrostrychnine is heated on the water bath with hydriodic acid (sp. gr. = 1·96) and phosphonium iodide. Tetrahydrostrychnine *hydrochloride*, $C_{21}H_{26}N_2O_2,HCl$, forms small, slender needles, and dissolves in less than 3 parts of hot water; 26·5 parts of water are required at 20°, and the solution is neutral towards litmus. The *dihydriodide*, $C_{21}H_{26}N_2O_2,2HI + 2H_2O$, crystallises in pyramids, and loses water in a vacuum. The *methiodide*, $C_{21}H_{26}N_2O_2 + MeI + H_2O$, crystallises from hot water in elongated, thin, lustrous needles, and dissolves with difficulty in cold water. The *nitrosamine* is resinous, but yields a *hydrochloride* which crystallises from warm water in yellowish, lustrous prisms; reduction with zinc dust and acetic acid converts it into a base, which slowly reduces boiling Fehling's solution.

Strychnoline, $C_{20}H_{24}N{<}\genfrac{}{}{0pt}{}{CH_2}{\overset{|}{N}}$, obtained by reducing deoxystrychnine in amylic alcohol with sodium, crystallises from dilute alcohol in small, colourless needles melting at 175—178° to a viscous resin; it is scarcely soluble in water, and dissolves sparingly in ether, but alcohol, chloroform, and benzene dissolve it readily. The solutions in dilute hydrochloric and sulphuric acids become reddish, and finally brown, when exposed to air, ferric chloride and potassium dichromate giving magenta-red colorations; sodium nitrite produces a liquid having the colour of eosin. When the base is treated with concentrated sulphuric acid, it becomes deep red, and when gently heated yields a violet solution; the solution in concentrated nitric acid is magenta-red.

Dihydrostrychnoline, $C_{20}H_{26}N{<}\genfrac{}{}{0pt}{}{CH_2}{\overset{|}{N}}$, prepared by passing a current of electricity through a solution of deoxystrychnine in 50 per cent. sulphuric acid, crystallises from light petroleum in colourless prisms, melts at 129°, and boils at 267—270° under a pressure of 16 mm. It is very soluble in organic liquids, but dissolves sparingly in water, yielding a distinctly alkaline solution. A 3 per cent. solution in chloroform has the specific rotatory power $[\alpha]_D = +10·5°$. In colour reactions and physiological influence, the base resembles strychnidine. The *hydrochloride*, which crystallises in small needles, dissolves very readily in hot water, but more sparingly in cold; the *nitrate* melts to a colourless liquid at 185° in a vacuum, becoming red at 180° in presence of air. The *methiodide* crystallises from water in white needles, and melts at 265°.

Strychnic and isostrychnic acids are indifferent to reducing agents.

Dinitrostrychnine hydrate, $C_{21}H_{22}N_2O_3(NO_2)_2$, is precipitated in

sulphur-yellow needles when sodium acetate is added to an aqueous solution of the nitrate, and contains $1H_2O$, which is removed at 165°; it is soluble in dilute mineral acids, and in alkalis, being precipitated from its solutions in the latter by carbonic anhydride. Alcoholic potash develops a beautiful, violet coloration, but the substance does not give the strychnine reaction with concentrated sulphuric acid and potassium dichromate. The *nitrate* (cacostrychnine), prepared by heating strychnine with 40 parts of 5 per cent. nitric acid, separates from the latter as a golden yellow, crystalline powder, which chars when heated.

Dinitroisostrychnic acid, $C_{21}H_{22}N_2O_3(NO_2)_2$, is a microcrystalline, sulphur-yellow substance, insoluble in water and in alcohol, but forming a red solution in alkalis; the *sulphate* crystallises in golden-yellow prisms; the *nitrate*, obtained by heating isostrychnic acid with 40 parts of 20 per cent. nitric acid during 20 hours, forms a dark yellow, microcrystalline powder, which chars when heated; alcoholic potash develops a violet coloration.

Dinitrostrycholcarboxylic acid, $C_{10}H_5N_3O_8$, is prepared by heating strychnine with 40 parts of 20 per cent. nitric acid during 72 hours in a reflux apparatus, evaporating the liquid to a syrup, and treating this with boiling concentrated nitric acid; it crystallises from concentrated nitric acid in prisms, and from alcohol in needles containing the solvent, which is removed below 110°. It melts at about 300°, liberating carbonic anhydride, and yielding dinitrostrychol; the acid dissolves somewhat readily in hot water, and crystallises in needles. An intense violet coloration is produced when the solution in sodium carbonate is treated with hydrogen sodium sulphite. The *potassium* salt crystallises in pale yellow needles, and detonates without melting when heated; it dissolves in 50 parts of boiling water. The *sodium* salt is more readily soluble, the solution yielding precipitates with lead acetate, and the chlorides of barium, calcium, iron, copper, and cobalt.

Diamidostrycholcarboxylic acid, $C_{10}H_9N_3O_4$, prepared by reducing dinitrostrycholcarboxylic acid with tin and hydrochloric acid, forms microscopic prisms, dissolving in ammonia, alkalis, and warm hydrochloric acid; the solutions are extremely sensitive towards oxidising agents, and quickly become red or brown when exposed to air. The *hydrochloride* crystallises from hot, hydrochloric acid in colourless prisms.

Dinitrostrychol, $C_9H_5N_3O_6$, produced on heating dinitrostrycholcarboxylic acid with 10 parts of water in sealed tubes at 200—210°, crystallises in slender needles; it becomes brown at 250—270°, and melts at about 284°, forming a brown liquid which slowly evolves gas. The alcoholic solution is neutral towards methyl-orange, and acid towards litmus. The *potassium* derivative forms minute needles, and the *dibarium* derivative contains $1H_2O$; the *methylic ether* is a brownish, crystalline powder, which melts at 196° and sublimes at higher temperatures.

Trinitrostrychol, $C_9H_4N_4O_8$, is formed from dinitrostrycholcarboxylic acid under the influence of fuming nitric acid, and dissolving somewhat readily in hot water, crystallises in colourless, glistening plates

as the liquid cools; it becomes brown at 205°, and melts at 215—218° (uncorr.). The aqueous solution is pale yellow, and has an acid action on litmus and methyl-orange. The *sodium* derivative dissolves very readily in hot water, and much more sparingly in cold water, forming a neutral solution. M. O. F.

Partial Racemism. By ALBERT LADENBURG and GUIDO DOCTOR (*Ber.*, 1898, 31, 1969—1971).—Strychnine racemate,

$$C_4H_6O_6,2C_{21}H_{22}N_2O_2,6\frac{1}{2}H_2O,$$

differs entirely in its properties from the corresponding salts of dextro- and lævo-tartaric acid, and also from a mixture of these, and is therefore to be regarded as a chemical individual. This is shown by the melting point, water of crystallisation, solubility, and density as given in the following table.

	Sp. gr. at 20°.	Solubility at 20°	Solubility at 40°	Melting point.	Water of crystallisation.
Racemate ...	1·4696	2·45	3·69	222°	$6\frac{1}{2}$ molecules
d-Tartrate...	1·5429	2·03	3·10	228	7 ,,
l-Tartrate ...	1·6080	1·7	2·05	242	$3\frac{1}{2}$,,

A. H.

Atropine Periodides and Mercuriodides. By HARRY M. GORDIN and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1898, 20, 329—338. Compare Jörgensen, *J. pr. Chem.*, 1871, [ii], 3, 329).—An *enneaiodide*, $C_{17}H_{23}NO_3,HI,I_8$, can be obtained under suitable conditions, which are given in detail in the paper. To obtain it in a crystalline form, it is first washed with a little cold alcohol to remove traces of free iodine and then dissolved in warm alcohol, from which it crystallises in dark-green prisms and leaflets; it is sparingly soluble in ether, chloroform, benzene, or carbon bisulphide, insoluble in water, and is decomposed when heated with water, and also on treatment with concentrated solutions of potassium iodide. At 90°, it begins to give up iodine, and melts to a dark liquid at 140°. One-ninth of the total iodine is firmly combined, whilst eight-ninths is easily removed by reducing agents, such as sulphurous anhydride or sodium thiosulphate.

The periodides are most readily obtained by using chloroform as a solvent. On adding atropine (20 grams) to a warm solution of iodine (30 grams) in chloroform (500 c.c.), the enneaiodide crystallises out in shining, dark-green crystals; the mother liquor gives several successive crops of the dark-blue *pentiodide*, and finally a crop of the brownish-red tri-iodide. The periodides readily give double salts with mercuric iodide; one may be obtained by shaking the alcoholic solution of the periodide with mercury and gently warming the mixture; it has the composition $C_{17}H_{23}NO_3,HI,HgI_2$, forms yellow crystals, melts at 89—90°, is sparingly soluble in ether or chloroform, moderately in hot water, and very readily in warm alcohol. If a solution of this compound in dilute alcohol is treated with an excess of potassium

iodide, a compound, $(C_{17}H_{23}NO_3,HI)_2HgI_2$, is obtained; it crystallises in white, silky needles melting at 98—99°, and is readily soluble in warm alcohol or hot water.

The formation of atropine enneaiodide affords a convenient method for estimating the strength of atropine solutions by adding excess of a standard solution of iodine, and titrating back with standard sodium thiosulphate. The method is only successful when extremely dilute solutions of atropine are employed, as otherwise a resinous mass is obtained. J. J. S.

Soluble Compound of Hydrastine with Monocalcium Phosphate. By THOMAS H. NORTON and H. E. NEWMAN (*J. Amer. Chem. Soc.*, 1897, **19**, 838—840).—When hydrastine is triturated with a saturated solution of monocalcium phosphate, a portion of it enters into solution, the amount dissolved increasing with the duration of trituration. At the end of six weeks, the proportion of hydrastine to calcium phosphate corresponds with the formation of a salt of the composition $2Ca(H_2PO_4)_2,3C_{21}H_{21}NO_5$. No definite salt could, however, be isolated from the solution, a resinous mass being left on evaporation. A. H.

Mandragorine. By HERMANN THOMS and M. WENTZEL (*Ber.*, 1898, **31**, 2031—2037. Compare Clouzel, *Un. Pharm.*, 1885, 264; Richardson, *Pharm. Journ. and Trans.*, 1888, 938, and 1049; Ahrens, Abstr., 1889, 1074, 1222).—Five grams of Ahrens' alkaloid (m. p. 79°) was dissolved in hydrochloric acid and the solution fractionally precipitated five times with gold chloride, 20 c.c. of a solution of 6 grams of gold chloride in 100 c.c. of water being used for each precipitation. The five fractions thus obtained exhibited, both macroscopically and microscopically, such differences that it was evident that the original alkaloid must have been a mixture. By repeated crystallisation of the different fractions from dilute hydrochloric acid, about 90 per cent. of the original precipitates was obtained in the form of large plates melting at 163—164°. These proved to be identical in every respect with hyoscyamine aurochloride, and the base obtained from them exhibited all the properties of hyoscyamine.

Mandragorine is thus a mixture of bases, the chief constituent of which is hyoscyamine. J. J. S.

Preparation of Cholic Acid, and its Behaviour towards Reducing Agents. By FRITZ PREGL (*Pflüger's Archiv.*, 1898, **71**, 303—317).—The author describes in detail the method he has found to yield the best results for the preparation of cholic acid from bile. On repeating Destrem's experiments (Abstr., 1879, 333) on the distillation of cholic acid with zinc dust, he found that the product consists of several non-separable hydrocarbons, which are decomposed when distilled under reduced pressure; no definite substance could be obtained by treating the mixture either with bromine or with nitric acid.

On heating cholic acid (0·6 gram) with concentrated hydriodic acid (5 c.c.) and red phosphorus (1 gram) during 8 hours at 270°, a *product* was obtained which appeared to have the constitution $C_{24}H_{36}$; it was not, however, prepared in at all a pure state.

When a mixture of cholic acid (10 grams), amorphous phosphorus (100 grams), and hydriodic acid (b. p. 127°) is boiled for an hour, a white, pulverulent *substance* is obtained (compare this vol., i, 389), which readily dissolves in ether, benzene, acetone, and acetic acid, less easily in alkalis and cold alcohol, and is insoluble in water; it cannot be obtained crystalline, but when approximately pure, melts at 117—120°, and has the composition $C_{24}H_{40}O_2$; the author suggests that it is the monobasic acid, $CH_2{:}C_{20}H_{31}Me_2{\cdot}COOH$, corresponding to Mylius's formula, $OH{\cdot}CH{:}C_{20}H_{31}(CH_2{\cdot}OH)_2{\cdot}COOH$, for cholic acid. On adding mineral acids to its alkaline solution and boiling, a coarse-grained precipitate is formed, which appears to consist of an *anhydride* of the acid analogous to the so-called dyslysins.

On adding the acid $C_{24}H_{40}O_2$ to hot concentrated nitric acid, simultaneous oxidation and nitration occur, an amorphous trinitrobilianic acid, $C_{24}H_{31}N_3O_{14}$, being formed, which melts at 169—172°, dissolves in alkalis with a dark-red coloration, and yields a *silver* salt, $C_{24}H_{28}N_3O_{14}Ag_3$. When alcoholic potash is added to its solution in alcohol, a reddish-brown precipitate is produced which dissolves in excess of the alkali; in this respect, trinitrobilianic acid resembles bilianic acid, and, like the latter, it appears to yield a *phenylhydrazone*, although this is very ill-characterised. W. A. D.

Two Derivatives of Cholic Acid. By FRITZ PREGL (*Pflüger's Archiv.*, 1898, **72**, 266—272).—If the crude products of reduction of cholic acid are treated with zinc dust and acetic acid, the presence of the undesirable iodo-compounds is avoided, and the yield of the anhydride, $C_{48}H_{78}O_3$, greatly augmented. It can best be purified by repeated dissolution in alkali and reprecipitation with acid. The substance thus obtained is precipitated from the solution of its potassium salt by carbonic anhydride and exhibits Pettenkofer's bile acids reaction; it melts at 76—80°, and appears to be identical with Seńkowski's cholylic anhydride (this vol., i, 389), but the author considers that his own method of preparation is to be preferred to Seńkowski's, as the use of hydriodic acid of 127° boiling point ensures comparatively rapid reduction.

In opposition to the view of Seńkowski, the author brings forward evidence to show that the free acid is capable of existence; the precipitate, which is first produced on adding acid to the solution of the anhydride in dilute potash, is flocculent and readily soluble in cold alkali, but if heated cautiously at 50—60°, it becomes sandy and insoluble; as this change is effected at a temperature far below the melting point of the anhydride, it cannot be due to mere coagulation, but must mean conversion of the free acid into its anhydride.

Further experiments on the action of boiling concentrated nitric acid on the anhydride have given results differing somewhat from those first recorded (*loc. cit.*), and a *product* crystallising in aggregates of needles has at last been isolated.

Preparation of Bilianic Acid.—The following method of preparing bilianic acid differs from that of Mylius in that it ensures the further transformation of dihydrocholic acid, the intermediate product of oxidation of cholic acid. A mixture of cholic acid (20 grams),

potassium dichromate (40 grams), sulphuric acid (60 grams), and water (160 grams), is heated, as Mylius recommends, until the solution becomes green; the liquid is then cooled, and the product collected over thin gauze and reduced, by rubbing, to a fine state of division; it is once more heated on the water bath for fifteen minutes with a fresh mixture of 20 grams potassium dichromate, 30 grams of sulphuric acid, and 80 grams of water, and it is recommended that, in case any aggregation ensues, the mass should be re-collected and again rubbed down before the oxidation is proceeded with. After cooling, the product is separated, dissolved in excess of soda, digested on the water bath, and filtered from chromium oxide; the filtrate is acidified, and the precipitate of nearly pure bilianic acid collected, washed, dried, and crystallised from dilute acetic acid. In this way, 15—16 grams of bilianic acid, in shining prisms melting at 266°, may be obtained.

Bromine water does not act on bilianic acid at the ordinary temperature, but when heated with it at 110° under pressure, considerable quantities of bromine disappear; the product thus obtained, however, is resinous and unsuited for analysis. A. L.

Bile Acids. By Gotthard Bulnheim (*Zeit. physiol. Chem.*, 1898, **25**, 296—324).—Glycocholic acid can be prepared from ox-bile by shaking it with small amounts of ether and concentrated hydrochloric acid; the acid, which separates after a short time, is washed with water until free from chlorine, and then crystallised first from warm water and afterwards from dilute acetic acid. The yield of pure acid obtained in this way varies from 1·5—2 per cent. of the bile used.

Cholic acid, obtained from glycocholic acid according to Hartmann's directions (*Kolbe's Journal*, **19**, 307), forms prismatic crystals containing $1H_2O$, which, when placed in alcohol, change to small tetrahedra containing $1C_2H_6O$; the yield is from 62—70 per cent. of the theoretical. The author was unable to prepare cholesteric acid by the oxidation of cholic acid according to Tappeiner's directions (Abstr., 1879, 388).

Bilianic acid, $C_{24}H_{34}O_8 + 2H_2O$, obtained by oxidising cholic acid with potassium chromate and sulphuric acid, was purified by dissolving in absolute alcohol, and after treating the solution with hydrochloric acid, allowing it to stand in sunlight for some days. The diethylic bilianate thus formed was hydrolysed with barium hydroxide, and the bilianic acid produced crystallised from alcohol; it is easily soluble in acetic acid, ether, and alcohol, but almost insoluble in light petroleum. The anhydrous acid melts at 264° (uncorr.), and is dextrorotatory $[\alpha]_D = +76°$. The *silver* salt forms small needles, and the *potassium hydrogen* salt plates. Bilianic acid is stable towards oxidising agents, chromic acid only attacking it when concentrated and on boiling; hydrogen peroxide, potassium ferrocyanide, and hypobromite, appear to be without action, and a cold solution of potassium permanganate is only reduced after some time. It does not give Pettenkofer's reaction, but on gently warming with concentrated sulphuric acid a peculiar green fluorescence is produced.

Dehydrocholic acid, isolated from the oxidation products of cholic acid, crystallises from dilute acetic acid and melts at 232°. It does

not give Pettenkofer's reaction, but with sulphuric acid a green fluorescence is produced.

Cholanic acid crystallises from acetic acid in quadratic prisms melting at 286° (uncorr.), and is dextrorotatory; $[\alpha]_D = +113°$. Its normal ethylic salt gives a *phenylhydrazone* as a radiating, crystalline mass, and therefore cholanic acid must be assumed to be a ketonic acid; it is more stable towards permanganate than bilianic acid, which it otherwise resembles in its reactions.

No crystalline cholesteric acid could be obtained by the oxidation of pure bilianic acid with potassium permanganate, either alone or in acid solution; nor could Seńkowski's statement be corroborated (*Monatsh.*, **17**, 1) that cholic acid on oxidation with permanganate yields phthalic acid. A. W. C.

New Bile-substances. By Olof Hammarsten (*Zeit. physiol. Chem.*, 1898, **24**, 322—350).—The bile of the great shark (*Scymnus borealis*, Scoresby) does not yield a trace of cholesterol, and, although of a yellowish-brown colour, contains neither bilirubin nor urobilin. The mixture of sodium salts obtained by precipitating the bile acids with lead acetate, and decomposing the precipitate with sodium carbonate, although responding in a striking manner to Pettenkofer's reaction and the fluorescence test, was found to contain no glycocholic or taurocholic acid. It consisted, instead of the salts, of at least two acids containing sulphur, which differ from taurocholic acid in losing the whole of their sulphur in the form of sulphuric acid when boiled with alkalis or acids; from this they would appear to be acid ethereal sulphates, and the names α- and *β-scymnolsulphuric acid* given to them indicate their character. *Sodium α-scymnolsulphate* was precipitated from a 3 per cent. aqueous solution of the mixed sodium salts by adding an equal volume of 40 per cent. aqueous potash; it was purified by repeating this process, and was freed from potassium hydroxide by dissolving in water, nearly neutralising with sulphuric acid, saturating with carbonic anhydride, evaporating to dryness, and extracting the salt with alcohol. The pure substance is quite white, contains 5·346 per cent. of sulphur, and produces a characteristic indigo-blue coloration when dissolved in 25 per cent. hydrochloric acid; it is easily soluble in ethylic and methylic alcohols, only sparingly in acetone, and insoluble in benzene. It can be dried at 120—125° without decomposition, but decomposes slightly at 130°. Its aqueous solution is stable, and produces no precipitate with barium chloride; the whole of the sulphur is removed, however, as sulphuric acid when the solution is boiled with dilute hydrochloric acid. When the hydrolysis is effected by barium or potassium hydroxide, a crystalline substance, *α-scymnol*, $C_{27}H_{46}O_5$ or $C_{32}H_{54}O_6$ is produced, which melts at 100—101°, and is sparingly soluble in water and benzene; it easily dissolves, however, in alcohol, ether, acetone, and warm chloroform, and can be obtained in globular aggregates of needles by carefully diluting its solution in acetic acid or in alcohol. It gives Pettenkofer's reaction and the fluorescence test for cholic acid, and produces the same coloration with hydrochloric acid as sodium α-scymnolsulphate;

it resembles cholesterol in responding to Schiff's test, and that of Liebermann and Blanchard, but fails to give Salkowski's reaction.

From the composition of α-scymnol, that of sodium α-scymnolsulphate is probably $C_{32}H_{53}O_5 \cdot SO_4Na$ or $C_{27}H_{45}O_4 \cdot SO_4Na$; it was impossible to discriminate by analysis between these formulæ, since the salt could never be obtained in a sufficiently pure state; it always contained from 0·17—0·3 per cent. of nitrogen, due to an impurity. The analysis of *barium α-scymnolsulphate*, which, on adding ether to the alcoholic solution, separates as a white powder readily soluble in water, gave numbers agreeing with either of the formulæ $(C_{27}H_{45}O_4 \cdot SO_4)_2Ba + 4EtOH$ or $(C_{32}H_{53}O_5 \cdot SO_4)_2Ba$, but owing to lack of material, it was impossible to decide between them.

On hydrolysing sodium α-scymnolsulphate with hydrochloric acid, a resinous product is obtained which possibly consists of a mixture of two *dyslysins*, having the formulæ $C_{27}H_{44}O_4$ and $C_{27}H_{42}O_3$, if that of α-scymnol be assumed to be $C_{27}H_{46}O_5$.

Sodium β-scymnolsulphate was not separated in a pure state from the α-salt, which it closely resembles; it differs from the latter in being more soluble in 20 per cent. potash, and in giving a green coloration when dissolved in 25 per cent. hydrochloric acid. There appears also to be present, in very small quantity, in the crude mixture of α- and β-salts, a third substance, a *γ-salt*, which differs from them in producing a precipitate with copper sulphate, lead acetate, and barium chloride, and in yielding an *acid* which is sparingly soluble in water; the γ-salt, like the α- and β-salts, contains no nitrogen, and gives the Pettenkofer reaction.

When the crude mixture of α- and β-salts is hydrolysed with potash, there is produced, in addition to α-scymnol, an amorphous substance, *β-scymnol*, $C_{29}H_{50}O_5$, which is probably its next higher homologue; it produces the same coloration with 25 per cent. hydrochloric acid as sodium β-scymnolsulphate, and like the latter gives Pettenkofer's reaction. W. A. D.

Urobilin. By JOHN L. W. THUDICHUM (*Virchow's Archiv.*, 1898, **153**, 154—158).—This paper is largely polemical in relation to the work of Garrod and Hopkins. What they call urobilin is regarded as the omicholin previously described by the author. W. D. H.

Urocaninic Acid. By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1898, **24**, 399—409).—A crystalline sediment from the urine of a dog was found to consist of urocaninic acid (compare Jaffé, Abstr., 1875, 478 and 1187); the author confirms Jaffé's formula, $C_{12}H_{12}N_4O_4 + 4H_2O$, for the latter, and points out that it does not melt sharply at 212—213°, but indefinitely at a somewhat higher temperature, which depends on the rapidity of the heating. One hundred c.c. of water dissolves, at 17·4°, 0·15 gram; at 18·7°, 0·16 gram; at 50°, 0·77 gram; and at 63°, 0·96 gram of anhydrous urocaninic acid. *Barium urocaninate*, $C_{12}H_{10}N_4O_4Ba + 2H_2O$, crystallises from water in tufts of slender needles.

No well-defined decomposition products could be obtained by acting on urocaninic acid with either oxidising or hydrolytic agents; in many

cases, no action at all took place. Bromine acts additively on urocaninic acid dissolved in acetic acid, a *dibromide*, $C_{12}H_{12}N_4O_4Br_2$, being formed, which, when dissolved in water or alcohol, decomposes into hydrogen bromide, urocaninic acid, and the product, $C_7H_6Br_4N_2O_4$, described below.

On passing bromine vapours into urocaninic acid suspended in water until the colour of the bromine ceases to be discharged, carbonic anhydride is evolved, and ammonium bromide formed, together with two distinct decomposition products. The first of these, *bromurocanidine*, $C_7H_5N_4Br_5$, is insoluble in water, ether, chloroform, benzene, and light petroleum, but easily soluble in methylic or ethylic alcohols, acetic acid, and ethylic acetate; when heated, it softens at 125°, and melts at 133°; on reduction with zinc dust and acetic acid, it yields a crystalline *substance* which contains no bromine. The second decomposition *product* of urocaninic acid, $C_7H_6Br_4N_2O_4$, crystallises from ether in four-sided prisms, is easily soluble in water and alcohol, but insoluble in chloroform, benzene, and light petroleum.

Jaffé's formula, $C_{11}H_{10}N_4O,H_2PtCl_6$, for the platinochloride of urocanine is confirmed; since urocanine gives the reactions of a xanthine derivative, and produces the same physiological effects as heteroxanthine and paraxanthine, it must be classed among the purine derivatives.

No urocaninic acid could be detected in human urine, either normal or arthritic. W. A. D.

Lysuric Acid and its Salts. By CLARA WILLDENOW (*Zeit. physiol. Chem.*, 1898, **25**, 523—550).—Lysuric acid, prepared from the pure barium salt, crystallises from dilute alcohol and melts at 144—145° (compare Abstr., 1896, i, 268). The *acid barium* salt, $2(C_6H_{12}Bz_2N_2O_2) + (C_6H_{11}Bz_2N_2O_2)_2Ba + 2H_2O$, crystallises in beautiful needles and melts at 144—148°, at which temperature it loses its H_2O. The *normal barium* salt, $(C_{20}H_{21}N_2O_4)_2Ba + 1\frac{1}{2}H_2O$, is a white, crystalline powder melting at 168°. The *acid sodium* salt is a white, crystalline mass melting at 108—109°, and contains $1H_2O$. The *acid strontium* salt crystallises in plates, melts at 137—138°, and contains $2H_2O$. The *normal strontium* salt is crystalline, and contains $1H_2O$. The *silver* salt, $C_{20}H_{21}N_2O_4Ag + \frac{1}{2}H_2O$, is a white, amorphous precipitate. A. W. C.

Chemical Nature of Diastase; Determination of its Activity by the Use of Soluble Starch; and the Occurrence of an Araban in Ordinary Diastase. By AUGUSTIN WRÓBLEWSKI (*Zeit. physiol. Chem.*, 1898, **24**, 173—223. Compare this vol., i, 500, and Osborne, this vol., i, 286).—The author deals at length with work which he has already briefly summarised (this vol., i, 54). In addition, a convenient apparatus is described for dialysing diastatic preparations in a continuous stream of water; and the following method is given for preparing soluble starch. Rice-starch (100 grams) is triturated with a small quantity of 2 per cent. caustic potash, left for 2—4 hours, and then diluted to 600—800 c.c. with the 2 per cent. alkali; the product is heated, first on the water bath until the liquid is quite thin, and subsequently over a bare flame for 30 minutes, and is then

slightly acidified with acetic acid; after precipitating with 95 per cent. alcohol, the product is twice redissolved and reprecipitated, and finally well washed with alcohol and ether. Soluble starch prepared in this way is a very white powder, which completely dissolves in water, but is insoluble in alcohol of greater concentration than 40 per cent.; it is entirely without action on Fehling's solution. With a mixture of copper sulphate and caustic soda, it gives the same reaction as Landwehr has stated to be characteristic of animal gum. A solution of soluble starch cannot be dialysed; it is precipitated by sodium, ammonium, and magnesium sulphate, and by tannin; in the latter case, however, on washing the precipitate with alcohol, the tannin is removed, and the residue becomes soluble in water. Soluble starch is not precipitated by phosphomolybdic or phosphotungstic acid, potassium mercury iodide, lead acetate either normal or basic, or mercuric chloride or nitrate. Soluble starch identical with the above can be prepared by heating rice-starch for 30 minutes with water to which 2 drops of 10 per cent. caustic potash has been added; if 10 drops of the alkali be employed, and the mixture heated during $4\frac{1}{2}$ hours, a product will be obtained which shows a slight cupric-reducing power.

By heating cane-sugar and inulin with very dilute alkalis, the author has brought about their partial hydrolysis; this explains the fact that pure inulin reduces Fehling's solution slightly after long heating. It appears, however, that hydrolysis by alkalis, which may be considered due to free OH-ions, is far slower than that due to acids, in which hydrogen-ions play part.

The following is the author's method of estimating diastatic activity. Two grams of soluble starch is dissolved in 100 c.c. of water; 0·01 gram of the diastase, dried at 60°, is dissolved in 10 c.c. of water, and left in contact at 40° during 8 hours, with 50 c.c. of the starch solution; at the end of this period, the solution is boiled to destroy the diastase, and the maltose formed estimated by Fehling's solution, using Allihn's method.

The paper concludes with a critical examination of the diastases prepared by other investigators, and a valuable bibliography is appended.

W. A. D.

Constitution of the Simplest Proteids. By ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1898, **25**, 165—189).—As, according to the earlier experiments of the author, the molecule of the complicated proteids contains an atom-complex similar to the protamine group, the more accurate chemical knowledge of the protamines should give an insight into the constitution of the albumin molecule. The author has therefore submitted the three protamines, sturine from the spermatozoa of the sturgeon, salmine from the salmon, and clupeine from herring sperm, to a closer investigation.

The protamine sulphates were prepared according to previous directions (*Zeit. physiol. Chem.*, 1895, **22**, 176) and freed from the last traces of nucleic acid by precipitating an aqueous solution with sodium picrate, dissolving the precipitate in excess of sulphuric acid, and shaking the solution with ether, to get rid of picric acid; the addition of alcohol to the evaporated solution causes the separation of the protamine sulphate,

Clupeine, $C_{30}H_{57}N_{17}O_6$.—The numerical results of the analysis of clupeine sulphate previously dried at 110—120° agree with the formula $C_{30}H_{57}N_{17}O_6,2H_2SO_4$. In the dry state, it is a white powder, easily soluble in warm water; on cooling the solution, a colourless, highly refractive oil is deposited, which dries on exposure to the air. Both this oil and clupeine sulphate are strongly lævorotatory.

Clupeine itself has a strongly alkaline reaction, gives a blue-violet biuret reaction, but no reaction with Millon's reagent or acetic and sulphuric acids. It is precipitated from neutral or faintly alkaline solution by potassium phosphomolybdate, molybdate, picrate, chromate or ferrocyanide, thus differing from peptones and propeptones (albumoses). Potassium tri-iodide, salts of the heavy metals, such as mercuric chloride, also bromine water, cause precipitation, the latter with formation of an unstable additive product. Clupeine, like other protamines, gives in ammoniacal solution a precipitate with coagulable albumin and albumoses.

Salmine.—The sulphate appears to have the formula

$$C_{30}H_{59}N_{17}O_7,2H_2SO_4,$$

or, in other words, only differs from clupeine sulphate in containing one more molecule of water. The author inclines to the belief that this arises from the different methods of drying the substances, and that in reality salmine and clupeine are identical; a supposition supported by the facts that the two substances have the same solubility in water, and the same optical activity and refractive index.

Sturine resembles salmine and clupeine markedly in properties, but is more easily soluble. The *sulphate* is precipitated from its solutions, on adding a few drops of ether, alcohol, or acetone, as an oil probably of the formula $4C_{36}H_{69}N_{19}O_7 + 11H_2SO_4$.

When the protamines are heated with dilute sulphuric acid, *protones* or peptones of the protamines are first obtained; these resemble the protamines in their properties, but their sulphates are more readily soluble, and they give none of the characteristic precipitates of the protamines.

By the further hydrolysis of the protamines the hexon bases, histidine, arginine, and lysine, are produced, the name hexon being retained for nitrogenous substances, and obtained by the decomposition of proteids containing six atoms of carbon.

In order to separate histidine from arginine and lysine, use is made of the fact that histidine carbonate, in absence of neutral alkali salts, is precipitated by mercuric chloride, whilst the carbonates of arginine and lysine are not. Arginine, when treated with silver nitrate, gives a basic substance containing silver, and as this is precipitated by alkali, it may thus be separated from lysine.

By the use of these methods, it becomes easy to prepare crystalline specimens of these hexon bases from the protamines, the exact details of which are given in the paper. Quantitative experiments show that, under these conditions, clupeine gives 1 molecule of histidine and lysine and 3 molecules of arginine, whereas sturine gives 1 molecule of histidine, 2 molecules of lysine, and 3 molecules of arginine.

As both protamines and proteids yield histidine, arginine, and lysine under certain conditions, it seems reasonable to suppose that the albumin molecule contains a protamine complex which yields these hexon bases on treatment with acids. To this complex are attached other groups which, on decomposition, yield the amido-acids of the fatty series, a third group gives tyrosine, and a fourth group gives the decomposition products containing sulphur. A. W. C.

Compounds of Proteids with Hydrochloric Acid, Sodium Hydroxide, and Sodium Chloride. By STEFAN BUGARSZKY and LEO LIEBERMANN (*Pflüger's Archiv.*, 1898, **72**, 51—74).—Whether acids, alkalis, and normal salts form actual compounds with albumin and similar substances, has long been a moot point with chemico-physiological workers. To solve the question, two methods hitherto not used for the purpose were tried; the first consisted in a measurement of the electromotive force of the supposed compounds; the second was the cryoscopic method of observing whether any lowering of the freezing point occurs. The conclusions arrived at by both methods are the same, namely, that hydrochloric acid is really chemically united to proteid substances (albumin, albumose, pepsin); that sodium hydroxide is also united to albumose and albumin, but that sodium chloride is not. W. D. H.

Behaviour of the Sulphur in Albumin free from Ash as Compared with that of Sulphur in the Halogen Derivatives of Albumin. By ERICH HARNACK (*Ber.*, 1898, **31**, 1938—1943. Compare Abstr., 1892, 645).—Although the conversion of egg-albumin into albumin free from ash by the author's method involves no loss of sulphur, this element is not in the same condition of oxidation in both compounds; whilst ordinary albumin rapidly blackens an alkaline solution of lead oxide, this agent is without influence on the ash-free albumin. Whether the oxidation undergone by sulphur in the conversion of egg-albumin into ash-free albumin is due to atmospheric oxygen or to the copper oxide, is at present undecided, but the author does not admit the general truth of Werigo's conclusion that metallic albuminates no longer contain unchanged albumin, because lead albuminate rapidly blackens a hot, alkaline solution of lead oxide; copper, zinc, and platinum albuminates, on the other hand, do not blacken lead oxide.

Although the proportion of sulphur in albumin is not altered by the introduction of halogens, the derivatives thus obtained do not blacken an alkaline solution of lead oxide (compare Hopkins and Pinkus, this vol., ii, 503). More vigorous action of halogens appears to eliminate groups containing sulphur in three stages, and the author concludes from this result that the molecule of albumin contains three atoms of sulphur, the minimum molecular weight being nearly 5,000; it remains questionable, however, whether it will not become necessary to multiply this number by two or three. M. O. F.

Effect of Minute Quantities of Acid on the Solubility of Globulin in Salt Solutions. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1897, **19**, 482—487).—It has been previously shown (Abstr., 1893, i, 380) that the principal globulin of

the seed of the castor-oil bean is partly insoluble in a saturated solution of sodium chloride and partly soluble therein, and that these two parts are alike in composition and differ but slightly in their reactions. More elaborate experiments have been made which confirm the above statement.

Experiments were also made by adding minute quantities of acetic acid (for example, 20 c.c. of 0·05 per cent. acetic acid) to the globulin and then dissolving by adding sodium chloride (2 grams); such a solution, when diluted with twice its volume of water, gave an abundant precipitate. A similar precipitate was obtained by saturating with sodium chloride. Similar solutions without the acetic acid gave no precipitates either on dilution or on saturation. The amount of acetic acid in all cases was so minute that the solutions gave a neutral reaction with litmus paper. In this manner, it has been shown that a quantity of acid too small to be detected with litmus or by analysis causes changes in the fractions soluble in saturated salt solution. Experiments have also been made with crystallised edestin from hemp seed, and similar results have been obtained. These changes are similar to those occurring naturally in the seeds and extracts of the castor-oil bean and sunflower, but whether such changes occur only through the influence of small quantities of acid is a point not yet settled. It has been found that edestin originally soluble in 10 per cent. sodium chloride solution, after keeping in stoppered bottles for from two to four years, becomes largely insoluble, and that its solutions are precipitated by saturating with salt. J. J. S.

Iodospongin, an Iodised Proteid Present in Ordinary Sponge. By Erich Harnack (*Zeit. physiol. Chem.*, 1898, **24**, 412—425).—The sponge employed by the author, after being cut into small pieces and extracted with dilute hydrochloric acid, contained only 0·35 per cent. of ash, and had an average composition.

C.	H.	N.	S.	I.	O.
48·51	6·30	14·79	0·73	1·50	about 28 per cent.

When left with dilute sulphuric acid (sp. gr. = 1·29) for 8 days, most of the sponge material dissolved and a powdery substance separated; this was twice dissolved in dilute caustic soda, and twice precipitated with dilute sulphuric acid, and purified for analysis by dissolving in ammonia, precipitating with ammonium sulphate, and dialysing the product. The substance thus obtained has the composition $C_{56}H_{87}IN_{10}S_3O_{23}$; if in its preparation the sulphuric acid is replaced by hydrochloric acid, a product containing less sulphur is formed; this probably has the composition $C_{56}H_{87}IN_{10}S_2O_{20}$, although a complete analysis was not made, owing to the difficulty of its preparation. To the latter substance, the name *iodospongin* is given, the former probably being its *monosulphonic acid*. This when freshly prepared is colourless, but soon darkens to a brownish-black; it dissolves in alkalis, but is reprecipitated by acids or ammonium sulphate; it produces a black coloration with alkaline lead oxide, but fails to give the biuret test, the sugar reaction in presence of α-naphthol (Molisch), or Adamkiewicz's reaction.

Since the ratio of sulphur to iodine is the same in iodospongin as

in the original sponge material (2 atoms of sulphur to 1 atom of iodine), the author concludes that a portion of the molecule of the latter has been split off which contains the whole of the iodine and sulphur; this portion is almost exactly one-sixth of the weight of the total molecule. W. A. D.

Formation of Arginine from Elastin. By ALBRECHT KOSSEL and FR. KUTSCHER (*Zeit. physiol. Chem.*, 1898, **25**, 551—552).—Bergh and Hedin (this vol., i, 608) have recently stated that Kossel's hexon bases are not obtainable from elastin, and that therefore a new group of proteid-like substances must be provided in Kossel's new scheme of classification. In the present research, it is shown that elastin from the *ligamentum nuchæ* does yield a small amount of arginine (0·3 per cent.). This is the easiest of the hexon bases to prepare. There is, therefore, no reason to doubt that elastin contains a protamine nucleus. W. D. H.

Formation of Levulinic Acid from Nucleic Acid. By ALFRED NOLL (*Zeit. physiol. Chem.*, 1898, **25**, 430—433).—The nuclein of yeast and of pancreas yields a reducing carbohydrate. Such a substance, however, is not obtainable from nucleic acid, although Kossel and Neumann showed that by the action of sulphuric acid at a high temperature on the nucleic acid of the thymus, levulinic acid (with formic acid) is obtainable; this appears to indicate the existence in nucleic acid of a carbohydrate complex. In the present research, nucleic acid was prepared from the spermatozoa of the sturgeon, and Kossel's result was confirmed. W. D. H.

Mucin from an Ovarian Cyst. By CHARLES LEPIERRE (*Compt. rend.*, 1898, **126**, 1661—1664).—The gelatinous contents of an ovarian cyst, when boiled with water, filtered, and the filtrate acidified with acetic acid, yielded 4 per cent. of a *mucin* differing in some particulars from those hitherto described, and having the percentage composition: carbon, 49·2; hydrogen, 7·0; nitrogen, 12·6; sulphur, 0·94; mineral matter, 0·5; undetermined, 29·76. These figures show that the substance is allied to the mucins obtained from the submaxillary glands and from tendons. It is not affected by dilute alkalis (1 : 1000), but on warming with more concentrated solutions of potash or soda, a clear yellow solution is obtained which, on adding acetic acid, yields either no precipitate or else one which is dissolved by excess of the acid. It is not dissolved by dilute acids in the cold, but on heating it is hydrolysed into albumoses and a *carbohydrate* of the formula $C_6H_{12}O_6$. The latter, which is inactive and non-fermentible, readily reduces Fehling's solution, and forms an *osazone* crystallising in yellow needles, and melting at 164—165°. The aqueous solution of the mucin is not coagulated by heat, nor does it reduce Fehling's solution; it is precipitated by neutral salts, tannin, mercuric chloride, &c., but in no case is the precipitate dissolved by excess of the reagent. When treated with pepsin and dilute hydrochloric acid at 45°, the mucin is converted into a mixture of mucin-albumose and mucin-peptone, which may be separated by means of ammonium sulphate. N. L.

The Proteid of Hæmoglobin. By FRIEDRICH N. SCHULZ (*Zeit. physiol. Chem.*, 1898, **24**, 449—481).—Pure crystalline oxyhæmoglobin is conveniently prepared from horse's blood by adding sufficient ammonium oxalate to prevent coagulation, allowing the corpuscles to subside, and diluting the latter with twice their volume of water; on adding to the solution an equal volume of saturated ammonium sulphate, and cooling to 0°, the fibrinogen and globulin are precipitated, whilst the oxyhæmoglobin remains dissolved; the solution is filtered at 0°, and left to stand until the whole of the oxyhæmoglobin has separated. Thus prepared, the latter is perfectly free from methæmoglobin, and can be kept some time without change.

When a very small quantity of dilute hydrochloric acid is added to a solution of hæmoglobin, a brown precipitate is formed, which immediately dissolves in an excess of acid; on now adding alcohol ($\frac{1}{5}$ vol.), and shaking with ether, the whole of the colouring substance is removed by the latter, whilst a yellowish precipitate is thrown down from the alcoholic solution on the addition of ammonia. On dissolving this in very dilute acetic acid, precipitating with ammonia, filtering, and washing with absolute alcohol and ether, nearly pure *globin* is obtained. This contains C = 54·97, H = 7·20, N = 16·89, S = 0·42 per cent., and must be distinguished from Preyer's "globin" obtained from methæmoglobin. Its aqueous solution is not coagulated by heat; on adding a trace of ammonia, caustic soda, or sodium carbonate, a flocculent precipitate is produced, which dissolves in the slightest excess of the alkali; if, however, the aqueous solution of globin is acidified with hydrochloric acid, an excess of ammonia produces a permanent precipitate.

Globin gives the biuret, xanthoprotein, Millon's, and Adamkiewicz's reactions; like the acid albumins, it dissolves in dilute acids, and is precipitated unchanged on exactly neutralising the latter; it differs however, from them in not being coagulable by heat, and in the behaviour of its aqueous solutions towards small quantities of nitric and hydrochloric acids; these produce coagula which dissolve when the solutions are warmed, and are reprecipitated on cooling. This behaviour resembles that of the primary albumoses, although globin differs from these in being insoluble in dilute solutions of sodium chloride and ammonium sulphate. Globin is in its properties most closely allied to the histons of Kossel (Abstr., 1885, 572), and of Lilienfeld (Abstr., 1894, ii, 146); these, however, contain on the average 52·26 per cent. of carbon, 7·19 per cent. of hydrogen, and 18·46 per cent. of nitrogen, and have therefore a very different composition from globin. It is also noteworthy that, whereas Lilienfeld's histon, when intravenously injected, is capable of preventing the coagulation of blood subsequently withdrawn, globin exercises no such influence under similar conditions. When large quantities of globin are injected, the latter is found in marked quantity in the urine; in the author's opinion, the presence of histon in the urine (compare Kolisch and Burián, Abstr., 1897, ii, 112) can equally well be attributed to the red blood corpuscles as to the leucocytes.

The author's analyses of horse's hæmoglobin give C = 54·56; H = 7·15; N = 17·33; and S = 0·43 per cent.; these values agree closely with

those of Hoppe-Seyler and of Otto and Bücheler. It would seem that hæmatin and globin are not the sole products of the decomposition of hæmoglobin; a substance having the reactions of a primary albumose appears to be formed in small amount.

The globin obtained from the hæmoglobin of dog's blood appears to be identical with that from horse's hæmoglobin; the blood of the goose, however, yields a globin which possesses different properties, and is possibly a nucleohiston. W. A. D.

Hæmochromogen. By RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1898, **25**, 492—506).—Hæmochromogen was prepared by reducing an ammoniacal alcoholic solution of hæmatin with hydrazine hydrate in an apparatus from which both oxygen and moisture could be excluded; it is precipitated from solution by a mixture of alcohol and ether, as a red, amorphous substance, resembling red phosphorus in appearance. The following numbers are the mean of five analyses of this preparation: C = 63·83; H = 5·66; Fe = 9·25; N = 11·48; and O = 9·78. Unfortunately, as the formula of hæmatin is doubtful, these results cannot lead to any definite conclusion regarding the constitution of hæmochromogen.

When an ammoniacal solution of hæmochromogen is neutralised with acetic acid, a voluminous, brownish-red precipitate is obtained, which contains iron, and on redissolving in ammonium hydroxide, shows the characteristic spectrum of hæmochromogen.

Hæmochromogen appears to be the only product of the action of hydrazine hydrate on hæmatin; with oxyhæmoglobin and methæmoglobin the reaction goes further. As shown by the spectroscope, hæmoglobin is first formed in both cases, then hæmochromogen, and after a time the solution becomes completely decolorised. Curves are given comparing the extinction coefficients of a 0·0082 per cent. ammoniacal solution of hæmochromogen with a solution of hæmatin of like strength. A. W. C.